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EPA METHOD STUDY 28, PCB's IN OIL

by

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This report describes the experimental design and the results of the validation study for two analytical methods to detect polychlorinated byphenyls in oil. The methods analyzed for four PCB Aroclors (1016, 1242, 1254, and 1260), 2-chlorobiphenyl, and decachlorobiphenyl. The first method consisted of diluting the oil in hexane and analyzing by gas chromatography using an electrolytic conductivity detector in the separating with sulfuric acid extraction or with column chromatography, and analyzing by gas chromatography using an electron capture detector. Four oils types were used in this study: capacitor fluid, hydraulic fluid, transformer oil, and waste oil. Each oil was spiked at six concentration levels with comprised three Youden pairs. Capacitor fluid was spiked with Aroclor 1016, hydraulic fluid with Aroclor 1242 and 2-chlorobiphenyl, transfomer oil with Aroclor 1260 and decachlorobiphenyl, and waste oil with Aroclor 1254.

Statistical analyses and conclusions presented in this report are based on analytical data obtained by eighteen participating laboratories and two volunteer laboratories. The two methods are assessed quantitatively with respect to the precision and accuracy that can be expected for each. In addition, various aspects of the methods are discussed, including such topics as method detection limits, sample stability interferences, and qualitative assessment of the methods based upon comments by the participating laboratories.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL-Cincinnati) conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication of EMSL-Cincinnati, entitled: EPA Method Study 28, PCBs in Oils, reports the results of EPA's interlaboratory method study for the following regulated substances under the Toxic Substance Control Act:

Aroclor 1016
Aroclor 1242
Aroclor 1254
Aroclor 1260
2-chlorobiphenyl (2-monochlorobiphenyl (MCB))
decachlorobiphenyl (DCB)

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this evaluative study of assistance in monitoring and controlling pollution in the environment.

Robert L. Booth
Director, EMSL-Cincinnati

ABSTRACT

This report describes the experimental design and the results of EPA Method Study 28 for two analytical methods to detect polychlorinated biphenyls (PCB's) in oil. The methods analyze for four PCB Aroclors (1016, 1242, 1254, and 1260), 2-chlorobiphenyl (2-MCB), and decachlorobiphenyl (DCB). The first method consists of diluting the oil in hexane and analyzing by gas chromatography using an electrolytic conductivity detector in the halogen mode. The second method consists of diluting the oil in hexane, cleaning/separating with sulfuric acid extraction or with column chromatography, and analyzing by gas chromatography using an electron capture detector. Four oil types were tested in this study: capacitor fluid, hydraulic fluid, transformer oil, and waste oil. Each oil was spiked with six concentration levels of PCBs which constituted three Youden pairs. Capacitor fluid was spiked with Aroclor 1016, hydraulic fluid with Aroclor 1242 and 2-MCB, transformer oil with Aroclor 1260 and DCB, and waste oil with Aroclor 1254.

Statistical analyses and conclusions presented in this report are based on analytical data obtained by eighteen participating laboratories and two volunteer laboratories. The two methods are assessed quantitatively with respect to the precision and accuracy that can be expected for each. In addition, various aspects of the methods are discussed, including such topics as sample stability, method detection limits, and qualitative assessment of the methods based upon comments by the participating laboratories.

This report is submitted in fulfillment of Contract 68-03-3006 by Versar Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1981 to December 1981, and work was completed as of May 1984.

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SECTION 1

INTRODUCTION

In 1976 polychlorinated biphenyls became regulated substances under the U.S. Toxic Substances Control Act (TSCA) (1). In support of Section 6 (e) of TSCA, Final Rules Prescribing Requirements for Disposal and Marking of PCB's and PCB-Containing Materials, an interlaboratory study was conducted for two test procedures for the analyses of PCB's in oil. The PCB's under study were Aroclor 1016, Aroclor 1242, Aroclor 1254, Aroclor 1260, 2-chlorobiphenyl (2-MCB) and decachlorophenyl (DCB).

The study required the analyses of four types of PCB-spiked oils by 20 laboratories. The methods evaluated in this study are described in the EPA Draft Method "The Analysis of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils" (revised June 1981) (2). This report is the result of the collaborative study of the two methods for analyzing PCB's in oils.

SECTION 2

SUMMARY

The gas chromatographic methods evaluated in this study are based upon Hall electrolytic conductivity detection (HECD) and electron capture detection (ECD). The HECD method requires diluting the oil sample and analyzing by GC. The ECD method requires diluting the oil, subjecting it to cleanup, and analyzing the extract by GC. Four oil categories and six PCB compounds were used in the method study. The oils were each spiked with PCBs at six different concentrations which composed three Youden pairs. Measured values for all concentrations were compared and statistically evaluated.

The accuracy of the HECD and ECD methods was determined by plotting the weighted linear regression of the mean recovery (X) versus the true concentration (T). The precision of the HECD and ECD methods was determined by plotting the weighted linear regression of the standard deviation (overall or single-analyst) versus mean recovery. The overall method precision (S) is a measure of the systematic and random variability including bias due to instrument calibration, operator technique, and equipment variability across laboratories. The single analyst precision (Sr) is a measure of the random variability due to instrument calibration and operator technique in a single laboratory.

The regression equations for accuracy, overall standard deviation, and single-analyst standard deviation are shown in Table 1.

In addition to summarizing the accuracy and precision of the methods for PCB's in oils, the following conclusions were made based upon the data:

TABLE 1. SUMMARY OF ACCURACY AND PRECISION REGRESSION EQUATIONS

Oil/PCB	$\bar{X}$, mg/kg	S, mg/kg	S_r, mg/kg
Capacitor Fluid/1016 (33-492 mg/kg)			
HECD	$\bar{X} = 0.86T + 1.21$	$S = 0.23\bar{X} + 0.90$	$S_r = 0.09\bar{X} + 4.98$
ECD	$\bar{X} = 0.81T + 3.10$	$S = 0.35\bar{X} - 2.70$	$S_r = 0.24\bar{X} - 1.86$
Hydraulic Fluid 1242 (39-492 mg/Kg)			
HECD	$\bar{X} = 0.89T - 4.28$	$S = 0.12\bar{X} + 2.50$	$S_r = 0.08\bar{X} + 3.29$
ECD	$\bar{X} = 0.92T - 5.87$	$S = 0.13\bar{X} + 5.45$	$S_r = 0.11\bar{X} - 0.67$
Hydraulic Fluid/2-MCB (41-1018 mg/kg)			
HECD	$\bar{X} = 0.97T - 13.00$	$S = 0.16\bar{X} + 1.74$	$S_r = 0.13\bar{X} - 0.40$
ECD	$\bar{X} = 0.88T - 5.35$	$S = 0.32\bar{X} + 2.42$	$S_r = 0.24\bar{X} + 0.73$
Transformer Oil/1260 (32-392 mg/kg)			
HECD	$\bar{X} = 1.02T - 2.62$	$S = 0.15\bar{X} + 5.97$	$S_r = 0.11\bar{X} + 3.50$
ECD	$\bar{X} = 1.04T - 4.46$	$S = 0.11\bar{X} + 2.14$	$S_r = 0.04\bar{X} + 1.89$
Transformer Oil/DCB* (0.37-16.6 mg/kg)			
HECD	$\bar{X} = 1.63T - 0.20$	$S = 0.74\bar{X} - 0.14$	$S_r = 0.12\bar{X} + 0.08$
ECD	$\bar{X} = 1.26T - 0.09$	$S = 0.55\bar{X} - 0.06$	$S_r = 0.39\bar{X} - 0.07$
Waste Oil/1254 (46-461 mg/kg)			
HECD	$\bar{X} = 0.84T - 2.00$	$S = 0.17\bar{X} + 6.28$	$S_r = 0.09\bar{X} + 5.59$
ECD	$\bar{X} = 0.95T - 7.02$	$S = 0.12\bar{X} + 3.29$	$S_r = 0.09\bar{X} + 2.07$

X = Mean Recovery
S = Overall Method Precision
S_r = Single-Analyst Method Precision
T = True Value for the Concentration
* = See recalculated regression equations in text

- Laboratory ranking outliers test rejected 10 and 15 percent of the data for HECD and ECD methods, respectively. The Thompson T-test rejected four percent of the data for both detection methods. Total percentage of outliers rejected for the entire inter-laboratory study was 16.5 percent.

- At a concentration level of 50 mg/kg of PCB in oil, the HECD and ECD analytical methods give comparable accuracy. In several instances, the overall and single-analyst precision was either smaller or larger for the HECD and ECD methods depending upon the aroclor and oil type.

- Statistical summaries of the HECD and ECD methods indicated, for the most part, a pronounced negative bias. The HECD and ECD methods for DCB show a pronounced positive bias which was attributed to the data of four participants. Rejection of these extreme data resulted in more realistic statistics and regression equations.

- For the DCB analyses, it is imperative, especially at low concentrations, to optimize the oven temperature to assure good peak geometry/resolution. Otherwise, integration of the peak area will result in a large positive bias and poor precision.

- A comparison of the HECD and ECD methods for PCB's in oils using the IMVS multiplicative model indicated no statistically significant difference.

- The ECD MDL is consistently lower than that for the HECD method. The HECD detection limit is matrix dependent and varies with oil type.

SECTION 3

DESCRIPTION OF STUDY

TEST DESIGN

The interlaboratory study was conducted to measure the precision and accuracy of USEPA's analytical methodologies for PCB's in oil. The statistical framework upon which this model was built is based on a form of the analysis of variance applying the approach and methods of W.J. Youden (3). The model is recommended by ASTM (4) in Standard Practice D2777-77 "Determination of Precision and Bias of Methods of Committee D-19 on Water." In the Youden approach to validating an analytical method, pairs of samples of similar but different concentrations are analyzed in the matrix of interest. The pair of concentrations is referred to as a unit block or as a Youden pair.

A summary of the test design using Youden's nonreplicate technique to separate random and systematic components of uncertainty is given below:

1. Three Youden pairs were used for each parameter with the deviation from the mean of the pair being at least 5 percent but no more than 20 percent.

2. The three Youden pairs were spread across the working range of the method with the lowest level near the detection limit and the mid-level and highest level near the values critical for PCB control, as suggested by current regulatory statutes.

3. Analyses were performed by 20 laboratories for six parameters according to two methodologies.

4. Each sample was analyzed only once by each laboratory for each method.

SELECTION OF LABORATORIES

Over 70 laboratories throughout the United States were contacted by Versar Inc. for an indication of interest. The list of laboratories included labs which previously participated in USEPA method studies, performed analytical work for USEPA, or participated in the ASTM D-27 Cooperative Study for PCB's in transformer oil. In response to a request for proposal, 28 laboratories responded with cost and technical proposals. Two performance evaluation samples (waste oil spiked with Aroclor 1254 and hydraulic fluid spiked with Aroclor 1242 and 2-MCB) were sent to the laboratories for PCB analyses in order to demonstrate their technical competency using both the ECD and the HECD. Negotiations with the firms resulted in contracts with 19 laboratories. However, during the study one laboratory withdrew from the project due to other work demands. Two volunteer laboratories who did not have HECD's participated in the ECD method study, with one of the volunteers limiting his efforts to the waste oil category. The total interlaboratory study, therefore, included 20 laboratories, which are listed in Table 2.

TABLE 2. PARTICIPATING LABORATORIES

Acurex Corp. 485 Clyde Avenue Mountain View, CA 94042	Global Geochemical Corp. 6919 Eton Avenue Canoga Park, CA 91303
Analytics Lab P.O. Box 25249 1414 Rhodemiller Street Richmond, VA 23220	Hazelton 1500 Frontage Road Northbrook, IL 60062
Biospherics 4928 Wyaconda Road Rockville, MD 20852	Jacobs Laboratories 373 South Fair Oaks Avenue Pasadena, CA 91105
Centec Analytical Service P.O. Box 956 2160 Industrial Drive Salem, VA 24153	Lancaster Labs Inc. 2425 New Holland Pike Lancaster, PA 17601

(continued)

TABLE 2 (continued)

Century Environmental Testing Labs
1501 Grandview Avenue
Thorofare, NJ 08086

Eastern Analytical
RFD 2, Clinton Street
Concord, NH 03301

EN-CAS Laboratories
1409J South Stratford Road
Winston-Salem, NC 27103

Environmental Research Group
117 N. First Street
Ann Arbor, MI 48104

General Electric Co.
Gate 18, Store R-40, Bldg 29B
East Street
Pittsfield, MA 01201

Radian Corp.
8501 Mo-Pac Boulevard
P.O. Box 9948
Austin, TX 78766

McLean Research Laboratories
Dept. of Entomology
Cook College/Rutgers Univ.
New Brunswick, NJ 08903

Monsanto Research Corp.
Station B, P.O. Box 8
1515 Nicholas Road
Dayton, OH 45407

Northrop Services Inc.
12th & Marshall
Little Rock, AR 72202

O.H. Materials
6406 State Route 224 East
Findlay, OH 45840

Orlando Labs, Inc.
P.O. Box 19127
800 Humphries Avenue
Orlando, FL 32803

Switchgear Services Inc.
880 Market Street
Oregon, WI 53575

PERFORMANCE EVALUATION

Previous method studies by the USEPA have shown that more realistic results can be obtained if all participants fully understand the analytical procedures before undertaking the full study. In this study, an initial set of performance evaluation samples was used to familiarize the analyst with the analytical methodology and to prove their proficiency in PCB analysis. Each of the interested laboratories was sent two oil samples spiked at mid-level concentrations, instructions for analyses, a copy of the method, and data report sheets (Appendix A). The two oils were selected such that the hydraulic fluid would represent a routine oil matrix and the waste oil would be a complex matrix containing interfering compounds.

The results of these analyses were collected and statistically analyzed. A summary of the performance evaluation data is presented in Table 3. Two laboratories submitted outlier data. Versar Inc. worked with them and provided suggestions, guidance, and additional samples to improve their ability to operate the HECD accurately.

TABLE 3. PERFORMANCE EVALUATION DATA SUMMARY

			HECD Method		ECD Method	
Parameter	Matrix	True Value (mg/kg)	Mean Value* (mg/kg)	Standard Deviation (mg/kg)	Mean Value* (mg/kg)	Standard Deviation (mg/kg)
Aroclor 1254	Waste Oil	65	57	3.9	60	4.4
Aroclor 1242	Hydraulic Fluid	69	61	2.5	67	2.8
2-Chloro-biphenyl	Hydraulic Fluid	60	55	4.1	63	2.5

* Mean value excludes statistical outliers

Laboratories being evaluated were contacted to discuss analytical problems and to clarify any ambiguity in the analytical procedures. Most problems involved the electrolytic conductivity detector: blocking of the reactor tube, inadequate sensitivity or lack of response, limited linear range, and high reactor temperatures. A summary of all questions, comments, and suggestions, as well as an HECD troubleshooting guide from Tracor (the sole HECD manufacturer), was sent to all laboratories before the interlaboratory study commenced.

METHODOLOGY AND INSTRUCTIONS

The method for determining PCBs in various oil types, detailed in the USEPA Method "The Analysis of Polychlorinated Biphenyls in Transformer Fluids and Waste Oils," (2) was tested by twenty laboratories. Previous method studies in the literature reported difficulties in interpreting

results because too many variables were present. Therefore, to test only the methodology, detailed instructions were given which specified sample cleanup procedures, detector types, column packing material, and the source of calibration standards. The order in which the samples were to be analyzed was specified; to avoid data bias, each lab was assigned a different random order. A copy of the method study instructions and methodology are included in Appendix B.

SELECTION OF OILS

Fifty oil samples representing fluids analyzed for regulatory compliance were examined for use in the study. The capacitor fluid selected was an isopropyl biphenyl matrix. It is the most probable replacement fluid for PCB's in capacitors and was obtained from Sun Oil Company under the trade name Suresol 250. The hydraulic fluid was a petroleum-based oil obtained from Mobil Oil Company under the designation DTE 25. The mineral-oil based transformer oil was obtained from Calumet Refining Company under the trade name Caltran 60-0. The waste oil was a road oil obtained from a local distributor.

PREPARATION OF AMPULS

Oil samples were spiked with PCB's by the direct addition of precisely weighed amounts of pure compounds. The Aroclors were provided by USEPA from the USEPA Repository for Toxic and Hazardous Materials. 2-MCB and DCB were obtained from Ultra Scientific Corp. The spiked oils were shaken, rolled for eight hours on a ball mill, and allowed to sit at room temperature for three days. Samples were analyzed to assure that each spiked oil was homogeneous and that no gross preparation errors had been committed. Oil aliquots were transferred into 5-mL clear glass ampuls which had previously been washed and baked. Approximately 1.5- and 3-mL aliquots were ampuled for HECD and ECD analyses respectively. The filled ampuls were sequentially labeled and flame-sealed using a Model/HS1 Cozzoli Hand Sealing Machine. The PCB spike concentrations are listed in Table 4.

TABLE 4. PCB True Value* in mg/kg Oil

Oil	Compound	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6
Capacitor	Aroclor 1016	33.7	492.	114.	81.6	441.	41.8
Hydraulic	Aroclor 1242	492.	95.7	47.1	39.8	64.3	402.
	2-MCB	1018	438.	55.6	41.3	350.	847.
Transformer	Aroclor 1260	332.	68.5	38.7	392.	80.7	32.5
	DCB	11.2	3.86	0.55	16.6	5.71	0.37
Waste	Aroclor 1254	350.	56.1	38.6	71.7	461.	46.9

*The true value stated for a parameter is the actual value calculated by weight for that parameter.

STABILITY STUDY

An important consideration in any validation study is verification of the true values and stability of the spiked samples. Homogeneity was verified by randomly selecting three replicate ampuls from each concentration level immediately after ampuling and analyzing them on a gas chromatograph equipped with an ECD. Stability was verified by analyzing duplicate ampuls before the start of the interlaboratory study, two to four times during the study, and finally after the study was completed, covering a time span of eight months.

SECTION 4

TREATMENT OF DATA

The objective of this interlaboratory study was to obtain information about the accuracy and precision associated with measurements generated by the Method "The Analyses of Polychlorinated Biphenyls in Transformers Fluids and Waste Oils." This objective was met through the use of statistical analysis techniques designed to extract and summarize the relevant information about accuracy and precision from the data reported by the participating laboratories. The statistical techniques employed in the data reduction process are similar to the techniques suggested in the ASTM Standard Practice D2777-77.

The algorithms required to perform the statistical analyses have been integrated by USEPA into a system of computer programs referred to as Interlaboratory Method Validation Study (IMVS). The analyses performed by IMVS (5) include several tests for the rejection of outliers (laboratories and individual data points), summary statistics by concentration level for mean recovery (accuracy), overall and single-analyst standard deviation (precision), determination of the linear relationship between mean recovery and concentration level, determination of the linear relationship between the precision statistics and mean recovery, and a test for the effect of detector type on accuracy and precision.

REJECTION OF OUTLIERS

Spurious data points are always a part of any set of data collected during an interlaboratory test program. It is important to identify and remove these data points because they can lead to values of summary statistics which are not representative of the general behavior of the method. However, some erratic behavior in the data may be directly related

to some facet of the method under the study. Therefore, spurious data points should not be removed indiscriminantly, and any points that are removed should be clearly identified since further investigation of the analytical conditions related to the outliers might be of value. Data rejected as outliers for this study as a result of any of the following tests for outliers have been identified by the symbol "*" in the raw data tables.

Youden's Laboratory Ranking Procedure

In some cases the analytical values reported by a specific laboratory are so consistently high or low that a large systematic error may be attributed to that laboratory. These data are not representative of the method and should be rejected. Youden's [3] ranking test for outlying laboratories was applied separately to data from each of the oils used in this study. Since six PCB types and two detectors were used in this study, the laboratory ranking procedure was applied to these twelve different subsets of the data. Each laboratory ranking test was performed at the 5 percent level of significance.

The Youden laboratory ranking procedure requires a complete set of data from every laboratory within a given sample type. Missing data from laboratory i for sample type j were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory i for sample type j and concentration level C_k, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \epsilon_{ijk}$$

where β_j and γ_j are fixed parameters which determine the effect of sample type j, L_i is the systematic error due to laboratory i and ϵ_{ijk} is the random within laboratory error. Taking natural logarithms, it follows that

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_K + \ln L_i + \ln \epsilon_{ijk}$$

which is a linear regression model with dependent variable $\ln X_{ijk}$ and independent variable $\ln C_k$. (Details and justification for this model

are discussed in the section "Comparison of Accuracy and Precision Across Detector Types".)

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampuls in each sample type. The predicted values $\ell n\, X_{ijk}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $X_{ijk} = \exp(\ell n\, X_{ijk})$. (For complete details of this procedure see Reference [6]).

If the ranking test rejected a laboratory for a specific sample type, then all of the laboratory's data for that sample type were rejected as outliers. The rejected values were excluded from all the remaining analyses. In addition, after completion of the laboratory ranking procedure, the predicted values created to fill in for the missing data were rejected and excluded from further analyses for all laboratories.

Tests for Individual Outliers

The data remaining after the laboratory ranking procedure were grouped by PCB type. For each sample type, the data were broken down into twelve subsets defined by the six concentration levels (ampuls) used in the study and the two detectors. For each subset of the data, all missing, zero, "less than" and "nondetect" data were rejected. Next, the test for individual outliers constructed by Thompson [7], and suggested in the ASTM Standard Practice D2777-77, was applied to the data using a 5 percent significance level. If an individual data point was rejected based on this test, it was removed from the subset, and the test was repeated using the remaining data in the subset. This process was continued until no additional data could be rejected.

STATISTICAL SUMMARIES

Several summary statistics were calculated using the data remaining for each concentration level after the outlier rejection tests were performed. These summary statistics include: the number of retained data

points, the mean recovery, accuracy as a percent relative error, the absolute overall standard deviation, the percent relative overall standard deviation, the absolute single-analyst standard deviation, and the percent relative single-analyst standard deviation. The basic formulas used to calculate these statistics are presented below where $X_1, X_2, \ldots, X_n$ denote the values of the n retained data points for a specific concentration level.

Mean recovery ($\bar{X}$):

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i$$

Accuracy as a % Relative Error:

$$\%RE = \frac{\bar{X} - \text{True Value}}{\text{True Value}} \times 100$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2}$$

and

Percent Relative Overall Standard Deviation:

$$\%RSD = \frac{S}{\bar{X}} \times 100$$

The overall standard deviation S indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in an interlaboratory study. However, a measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by SR, was estimated for each Youden pair by

$$SR = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2}$$

where

m = the number of complete sets of Youden pair observations remaining after outliers have been removed,

$\bar{D}_i$ = the difference between the observations in the Youden Pair

and

$\bar{D}$ = average of the D_i values.

The percent relative single-analyst standard deviation was calculated by

$$\%RSD\text{-}SR = \frac{SR}{X^*} \times 100$$

where X^* is the average of the two mean recovery statistics corresponding to the two concentration levels defining the particular Youden pair.

These summary statistics provide detailed information on the accuracy and precision of the data obtained for each concentration level. One objective of the statistical analysis of the data is to summarize the information about accuracy and precision which is contained in the statistics.

It is often the case that a systematic relationship exists between the mean recovery (X) and the true concentration level (C) of the analyte in the sample. In addition, there are often systematic relationships between the precision statistics (S and SR) and the mean recovery (X). Usually these systematic relationships can be adequately approximated by a linear relationship (i.e., by a straight line). Once these straight lines are established, they can be used to conveniently summarize the behavior of the method within a sample type, and they can aid in comparing the behavior of the method across detector types. In addition, they can be used to obtain estimates of the accuracy and precision at any concentration level within the applicable range studied. They can also be used to predict the behavior of the method when used under similar conditions. These important relationships are discussed below.

STATEMENT OF METHOD ACCURACY

The accuracy of the method is characterized by the relationship of the mean recovery ($\bar{X}$) to the true concentration (C) of the analyte in the oil sample. In order to obtain a mathematical expression for this relationship, a regression line of the form

$$\bar{X} = a + b \cdot C \qquad (1)$$

was fitted to the data by regression techniques.

It is often the case that the true concentration values vary over a wide range. In such cases, the mean recovery statistics associated with the larger concentration values tend to dominate the fitted regression line producing relatively larger errors in the estimates of mean recovery at the lower concentration values. In order to eliminate this problem, a weighted least-squares technique was used to fit the mean recovery data to the true concentration values. The weighted least-squares technique was performed by dividing both sides of Equation (1) by C resulting in Equation (2)

$$\frac{\bar{X}}{C} = a \cdot \frac{1}{C} + b \quad . \qquad (2)$$

The (X/C) values were regressed against the (1/C) values using ordinary least squares to obtain estimates for the values of a and b. (This is equivalent to performing a weighted least-squares with weights $w = 1/C^2$; see reference [6], page 108 for details.) Equation (2) can easily be converted to the desired relationship given by Equation (1). The intercept (b) from Equation (2) becomes the slope (b) for Equation (1) and slope (a) from Equation (2) becomes the intercept (a) for Equation (1). Equation (1) can be used to calculate the percent recovery over the applicable range of concentrations used in the study.

The percent recovery is given by

$$\text{Percent Recovery} = \left[\frac{a + b \cdot C}{C}\right] \times 100 = \left[\frac{a}{C} + b\right] \times 100 \qquad (3)$$

If the absolute value of the ratio (a/C) is small relative to the slope (b) for concentration in the low end of the range of concentration levels used in the study, then the percent recovery can be approximate by b x 100. For example, suppose the true concentration values range from 25 µg/ℓ to 515 µg/ℓ, the fitted line is given by $X = 0.20 + 0.85 \cdot C$. The percent recovery would be approximated by (0.85) x 100 = 85% over the specified range of 25 µg/ℓ to 515 µg/ℓ.

If the absolute value of the ratio (a/c) is not small relative to the slope (b), then the percent recovery depends upon the true concentration (c), and it must be evaluated at each concentration value within the specified range.

STATEMENT OF METHOD PRECISION

The precision of the method is characterized by the relationships between precision statistics (S and SR) and mean recovery ($\bar{X}$). In order to obtain a mathematical expression for these relationships, regression lines of the form

$$S = d + e \cdot X \tag{4}$$

and

$$SR = f + g \cdot X^* \tag{5}$$

were fitted to the data.

As discussed previously with respect to accuracy, the values of $\bar{X}$ and X^* often vary over a wide range. In such cases the standard deviation statistics associated with the larger mean recovery values will dominate the regression lines. This will produce relatively larger errors in the estimates of S and SR at the lower mean recovery value. Therefore, a weighted least squares technique was also used to establish the values of the parameters d, e, f and g in Equations (4) and (5). The weighted least squares technique was performed by dividing both sides of Equation (4) by $\bar{X}$ resulting in Equation (6).

$$\frac{S}{\bar{X}} = d \cdot \frac{1}{\bar{X}} + e \quad , \tag{6}$$

and dividing both sides of Equation (5) by X* resulting in Equation (7)

$$\frac{SR}{X^*} = f \cdot \frac{1}{X^*} + g \quad . \tag{7}$$

The (S/X) values were regressed against the $(1/\bar{X})$ values and the (SR/X*) values were regressed against the (1/X*) values using ordinary least squares to obtain estimates for the parameters d, e, f, and g.

Equations (4) and (5) were obtained from Equations (6) and (7) in a manner similar to that discussed for mean recovery. The slope (d) for Equation (6) is the intercept (d) for Equation (4), and the intercept (e) for Equation (6) is the slope (e) for Equation (4). Similarly, the slope (f) for Equation (7) is the intercept (f) for Equation (5), and the intercept (g) for Equation (7) is the slope (g) for Equation (5).

Given Equations (4) and (5), the percent relative overall standard deviation and the percent relative single-analyst standard deviation are

$$\% \text{ RSD} = \left[\frac{d}{\bar{X}} + e\right] \times 100 \tag{8}$$

and

$$\% \text{ RSD-SA} = \left[\frac{f}{X^*} + g\right] \times 100 \tag{9}$$

respectively. If absolute values of the ratio $(d/\bar{X})$ is small relative to the slope (e), then the percent relative overall standard deviation can be approximated by (e x 100) over the applicable range of mean recovery values. Similarly if the absolute value of the ratio (f/X*) is small relative to the slope (g), then the percent relative single-analyst standard deviation can be approximated by (g x 100) over the applicable range of mean recovery values.

If the ratios $(d/\bar{X})$ and (f/X*) are not small relative to the slopes (e) and (f), then the percent relative standard deviations depend upon the values of the mean recovery statistics $\bar{X}$ and X*, and they should be evaluated separately for each value of $\bar{X}$ and X*.

COMPARISON OF ACCURACY AND PRECISION ACROSS DETECTOR TYPES

It is possible that the accuracy and precision of the Method "The Analysis of Polychlorinated Biphenyls in Transformer Fluid and Waste Oil" depend upon the type of detector being used. The summary statistics $\bar{X}$, S and SR are calculated separately for each concentration level within each PCB type with each detector. They can be compared across detector types in order to obtain information about the effects of detector type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome since there are 72 mean recovery statistics ($\bar{X}$) (6 concentrations x 6 PCB's x 2 detectors), 12 percent statistics (S) and 6 precision statistics (SR) calculated for each compound. Comparison of these statistics across concentration levels and across detector types becomes unwieldy. Second, the statistical properties of this type of comparison procedure are difficult to determine. Finally, due to variation associated with $\bar{X}$, S and Sr, comparisons based on these statistics can lead to inconsistent conclusions about the effect of detector type. For example, the HECD may produce a significantly lower value than the ECD for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach, described in detail in Reference [8], has been developed to test for the effects of detector type. This alternative approach is based on the concept of summarizing the average effect of detector type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of detector type is based on the following statistical model. If X_{ijk} denotes the measurement reported by laboratory i, for detector type j, and ampul k, then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \epsilon_{ijk} \qquad \begin{matrix} i = 1,2,\ldots, n \\ j = 1 \\ k = 1,2 \end{matrix} \qquad (10)$$

The model components β_j and γ_j are fixed parameters which determine the effect of detector type j on the behavior of the observed measurements (X_{ijk}). The parameter C_k is the true concentration level associated with ampul k. The model component L_i is a random factor which accounts for the systematic error associated with laboratory i. The model component ε_{ijk} is the random factor which accounts for the within laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data (X_{ijk}) and the true concentration level C_k through the use of the exponent γ_j on C_k. This makes the model more flexible in comparison to straight lines models. Second, as will be seen below, there is an inherent increasing relationship between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements (X_{ijk}). The expected value for the data modeled by Equation (10) is

$$E(X_{ijk}) = \eta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (11)$$

Precision is related to the variability in the measurements (X_{ijkl}). The variance of the data modeled by Equation (10) is

$$Var(X_{ijk}) = \left[\beta_j C_k^{\gamma_j}\right]^2 Var\,(L_i \cdot \varepsilon_{ijk}) \quad , \qquad (12)$$

which is an increasing function of C_k.

The accuracy and precision of the method for PCB analysis depend upon detector type through Equations (11) and (12) and the parameters (β_j) and (γ_j). If the (β_j) and (γ_j) vary with j (i.e., vary across detector type), then the accuracy and precision of the method also vary across detector type.

In order to determine if these parameters do vary across detector type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation (10) represents the basic model. However, taking natural logarithms of both sides of Equation (10), the following straight line regression model is obtained,

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_k + \ln L_i + \ln \epsilon_{ijk} \qquad (13)$$

which can be analyzed using standard linear model analysis techniques. The parameter $\ln \beta_j$ is the intercept and γ_j the slope of the regression line associated with detector type j. It is assumed that $\ln L_i$ is normally distributed with mean 0 and variance σ_L^2, and that $\ln e_{ijk}$ is normally distributed with mean 0 and variance σ_L^2, and that the $(\ln L_i)$ and $(\ln \epsilon_{ijk})$ terms are independent.

Based on Equation (13) the comparison of detector types reduces to the comparison of straight lines. The HECD is viewed as a control, and the remaining line (for the ECD) is compared directly to the line for the HECD.

Using the data on the log-log scale and regression techniques, the parameters $\ln \beta_j$ (and hence β_j) and γ_j can be estimated. The estimates are then used to test the null hypothesis that there is no effect due to detector type. The formal null and alternative statistical hypotheses H_0 and H_A are given by

$$H_0: \ln n_j - \ln n_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2$$

versus

$$H_A: \ln n_j - \ln n_1 = 0 \text{ and/or } \gamma_j - \gamma_1 = 0 \text{ for } j = 2$$

The test of null hypothesis H_0 against the alternative hypothesis H_A is based on an F-statistic derived from standard linear model theory. The probability of obtaining a value of an F-statistic as large a the value which was actually observed (F OBS), denoted by P(F > F OBS), as calculated under the assumption that H_0 is true. The null hypothesis H_0 is rejected in favor of H_A if P(F > F OBS) is less than 0.05.

If H_0 is rejected, then some linear combination of the differences $\ln - \ln \beta_1$ and $\gamma_j - \gamma_1$ is statistically different from zero. However, this does not guarantee there will be a statistically significant direct effect attributable to any specific detector type since the overall F test can be overly sensitive to minor systematic effect common to detectors. The effect due to a specific water type is judged to be statistically significant only if one of the differences $\ln \beta_j - \ln \beta_1$ and/or $\gamma_j - \gamma_1$ is statistically different from zero. This is determined by by checking the simultaneous 95 percent confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95 percent confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences $\ln \beta_j - \ln \beta_1$ or $\gamma_j - \gamma_1$ fails to include zero, then the statistical significance of the effect due to detector type has been established. However, establishment of a statistically significant effect due to detector type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the difference.

The interpretation of the differences involves comparing the mean recovery and standard deviation of the (X_{ijk}) data for each detector type to the mean recovery and standard deviation obtained for the HECD. These comparisons are made on a relative basis. The mean recovery for detector type j is given by Equation (11). The mean recovery for detector type j is compared to that for the HECD (j=1) on a relative basis by

$$\frac{E(X_{ijk})}{E(X_{i1k})} = \frac{\beta_j C_k^{\gamma_j} E(L_i \cdot \varepsilon_{ijk})}{\beta_1 C_k^{\gamma_1} E(L_i \cdot \varepsilon_{i1k})} = \frac{\beta_j}{\beta_1} C_k^{\gamma_j - \gamma_1} \qquad (14)$$

(The ratio of the standard deviations would be equivalent to Equation (14), and therefore the interpretation of the effect on precision is the same as that for the effect on mean recovery.)

The ratio in action (14) is a measure of the relative difference in mean recovery between detector type j and the HECD. It is comprised of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e. the constant bias), and (b) $C_k^{\gamma_j - \gamma_1}$ which depends upon the true concentration level (i.e. the concentration dependent bias). If $\gamma_j - \gamma_1$ is zero, then the relative difference in mean recovery is just β_j/β_1 which is independent of concentration level C_k. It can then be stated that the mean recovery of detector type j is (β_j/β_1) x 100 percent of the mean recovery for the HECD. If $\gamma_j - \gamma_1$ is not zero, then the mean recovery of detector type j is $((\beta_j/\beta_1) C_k^{\gamma_j - \gamma_1})$ x 100 percent of that for the HECD, and therefore depends upon the true concentration level C_k.

In order to illustrate these points consider the following example which compares at least five detector types. Suppose that a significant F-value has been obtained, and the confidence intervals for all the differences contain zero except for detector type 5. For detector type 5, the point estimate for $\ln \beta_5 - \ln \beta_1$ is -0.38 and the confidence interval for $\ln \beta_5 - \ln \beta_1$ is (-0.69, -0.07). The points estimate for $\gamma_5 - \gamma_1$ is 0.07, and the confidence interval for $\gamma_5 - \gamma_1$ is (-0.04, 0.18). In this case a statistically significant effect due to detector type has been established which involves only detector type 5. The practical significance of this effect is judged by considering Equation (14). The ratio of mean recoveries for detector type 5 and the HECD is given by

$$\frac{E(X_{15k})}{E(X_{11k})} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5 - \gamma_1} \tag{15}$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{Var(X_{11k})}{Var(X_{11k})}} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5 - \gamma_1} \tag{16}$$

Since the confidence interval for $\gamma_5 - \gamma_1$ contains zero this difference is assumed to be insignificant and is set to zero. Therefore Equations (15) and (16) reduce to β_5/β_1. The point estimate for $\ln \beta_5 - \ln \beta_1$ was -0.38.

Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for detector type 5 is estimated to be 68 percent of the mean recovery for the HECD. Similarly the standard deviation for the data for detector type 5 is estimated to be 68 percent of the standard deviation for the HECD. Since the 95 percent confidence interval for $\ln \beta_5 - \ln \beta$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for detector type 5 can be claimed to be from 50 percent to 93 percent of the mean recovery (standard deviation) for the HECD. The practical significance of the effect due to detector type 5 would depend upon the importance of a mean recovery (standard deviation) observed for the HECD.

SECTION 5

DISCUSSION AND CONCLUSIONS

STABILITY STUDY

Ampuls of each concentration of the spiked oils were randomly selected for analyses during the interlaboratory study. The concentrations determined experimentally by ECD were within the expected error of the values determined by weight. (Most values were within 20 percent of the gravimetrically determined values and, as expected for the ECD, were more often less than the spiked value. An occasional determination exceeded the 20 percent margin but was always within the standard deviation typical of these analyses, as measured historically and from the performance evaluation samples. Only the hydraulic fluid ampul #3 showed a consistently low concentration for the 2-MCB. The results of the stability and verity study are presented in Table 5.

OUTLIERS

All outlying data were reported back to the laboratories involved so that calculations and analytical conditions could be verified. No indication was given as to the nature of the rejection in order to avoid prejudicing the results. If an error was found, the corrected value was used in the data analysis. If no error was found, the values remained as reported.

Laboratory ranking was performed within each sample type for the six concentrations analyzed by each detector. Data which were biased consistently high or low were rejected for that sample type. Laboratory outliers are designated by a star in the "lab reject" column of the Raw Data Tables and are summarized in Table 6. Of all data, 10 percent was rejected as laboratory outliers by the HECD method and 15 percent by the

TABLE 5. RESULTS OF VERIFICATION AND STABILITY STUDY
(Results in mg/kg)

Parameter	Ampul	True Value	Initial Value	Mean Value[1]	RSD[2]	Mean Recovery[3]
Aroclor 1016 in Capacitor Fluid	1	33.7	32	30	17%	89%
	2	492.	490	440	9%	89%
	3	114.	110	110	6%	96%
	4	81.6	79	78	5%	96%
	5	441.	440	400	8%	91%
	6	41.8	37	38	13%	91%
Aroclor 1242 in Hydraulic Fluid	1	492.	490	470	4%	96%
	2	95.7	89	88	9%	92%
	3	47.1	40	30	5%	83%
	4	39.8	36	37	3%	93%
	5	64.3	64	65	8%	101%
	6	402.	390	435[4]	15%	108%
2-MCB in Hydraulic Fluid	1	1018.	980	970	3%	95%
	2	438.	420	390	16%	89%
	3	55.6	35[5]	34	3%	61%
	4	41.3	31	31	2%	75%
	5	350.	310	280[4]	15%	80%
	6	847.	810	850	4%	100%
Aroclor 1260 in Transformer Oil	1	332.	300	280	12%	84%
	2	68.5	59	52	10%	76%
	3	38.7	31	29	7%	75%
	4	392.	380	360	14%	92%
	5	80.7	63	58	7%	72%
	6	32.5	25	22	9%	68%
DCB in Transformer Oil	1	11.2	16	12	25%	107%
	2	3.86	4.4	4.1	5%	106%
	3	0.55	0.69	0.68	10%	124%
	4	16.6	20.	17	18%	102%
	5	5.71	5.9	5.8	3%	102%
	6	0.37	0.51	0.49	8%	132%
Aroclor 1254 in Waste Oil	1	350.	230[6]	280	11%	80%
	2	56.1	50	46	13%	82%
	3	38.6	35	28	25%	73%
	4	71.7	45[6]	58	17%	81%
	5	461.	230[6]	400[4]	8%	87%
	6	46.9	42	37	19%	79%

1. Mean value of ampuls analyzed before, during, and after the study (7-9 ampuls).
2. RSD = relative standard deviation.
3. Mean Recovery: mean value/true value.
4. Mean value excludes one outlier.
5. Initial value was low, but immediate reanalysis and entire stability study were very consistent.
6. Initial value was low. Immediate reanalysis gave acceptable results.

TABLE 6. LABORATORY OUTLIERS

Oil	PCB	Outlier Labs HECD	Outlier Labs ECD
Capacitor Fluid	1016	19	3,7,14,19,23
Hydraulic Fluid	1242	7,14,19	9,14,19
	2-MCB	7,11,13,14	13,14,23
Transformer Oil	1260	7,18	7,14,23
	DCB	None	None
Waste Oil	1254	14	12,14,22

ECD method. The greater occurrence of bias by the ECD method implies that laboratories introduce a consistent error during sample preparation.

Laboratory outliers were removed from the data before application of the Thompson T-test for the identification of individual outliers. Both the HECD method and the ECD method rejected four percent of all data as individual outliers; random error affected both methods equally.

A minimum of twelve good data sets were obtained for all parameters except the lowest Youden pair of DCB concentrations as analyzed by the HECD method. Several laboratories submitted nondetectable data for the DCB/HECD method, which was due to poor chromatographic conditions (low oven temperature). Therefore, these laboratories were sent new samples for analyses. All labs except one (who used a Model 310 HECD) submitted acceptable data after optimizing the chromatographic system and detector parameters. The instruments and detectors used by the laboratories are listed in Appendix C.

RAW DATA

A compilation of the raw data is presented in Appendix D. The tables are listed by compound with each laboratory's data presented by

detection method. Laboratory #2 only analyzed the waste oil by the ECD method: Laboratory #17 analyzed all samples by the ECD method only. Laboratory numbers 1, 6, 8 and 21 were not assigned. All laboratories were sent a copy of the computer entry of their data. They verified correct entry or indicated errors on a standard reply form.

STATISTICAL SUMMARIES

After rejection of outlier data, the retained data were characterized statistically. The USEPA computer program IMVS was used for all calculations. The Statistical Summaries are presented in Tables 7 through 12.

The statistical parameters included are:

a. n, Number of data points: number of laboratories submitting results which are not outliers.

b. T, True value, mg/kg: theoretical value of the ampul based on weighed quantity of chemical.

c. $\overline{X}$ bar, Mean recovery, mg/kg: mean value of the non-outlier data.

d. Accuracy as percent relative error: difference between mean recovery and true value as a percentage of the true value.

e. S, Overall standard deviation, mg/kg: standard deviation of X_i values.

f. Overall relative standard deviation, percent: standard deviation of X_i values as a percentage of $\overline{X}$.

g. S_r, single-analyst standard deviation, mg/kg: standard deviation for a given Youden pair (as described in the Statistical Treatment Section).

h. Single-analyst relative standard deviation, percentage: S_r as a percentage of $\overline{X}$.

TABLE 7. STATISTICAL SUMMARY OF ANALYSIS OF AROCLOR 1016 IN CAPACITOR FLUID

Statistical Parameter	HECD		ECD	
Low Youden Pair	1	6	1	6
Number of Data Points	17	17	14	14
True Value, mg/kg	33.70	41.80	33.70	41.80
Mean Recovery, mg/kg	30.52	36.69	32.31	34.60
Accuracy As % Rel Error	-9.44	-12.23	-4.13	-17.22
Overall Std Dev (S), mg/kg	7.32	9.98	7.85	11.10
Overall Rel Std Dev, %	24.00	27.21	24.31	32.09
Single Analyst Std Dev, (SR), mg/kg	7.43		6.80	
Single Analyst Rel Dev, %	22.12		20.31	
Medium Youden Pair	4	3	4	3
Number of Data Points	16	16	14	14
True Value, mg/kg	81.60	114.00	81.60	114.00
Mean Recovery, mg/kg	71.83	96.03	68.43	92.57
Accuracy As % Rel Error	-11.92	-15.76	-16.14	-18.80
Overall Std Dev (S), mg/kg	13.62	34.75	19.13	30.02
Overall Rel Std Dev, %	18.96	36.19	27.96	32.43
Single Analyst Std Dev, (SR), mg/kg	15.59		12.42	
Single Analyst Rel Dev, %	18.57		15.43	
High Youden Pair	5	2	5	2
Number of Data Points	17	16	14	14
True Value, mg/kg	441.00	492.00	441.00	492.00
Mean Recovery, mg/kg	382.18	429.56	376.00	404.21
Accuracy As % Rel Error	-13.34	-12.69	-14.74	-17.84
Overall Std Dev (S), mg/kg	80.83	87.06	161.27	114.38
Overall Rel Std Dev, %	21.15	20.27	42.89	28.30
Single Analyst Std Dev, (SR), mg/kg	29.69		105.61	
Single Analyst Rel Dev, %	7.31		27.07	

TABLE 8. STATISTICAL SUMMARY OF ANALYSIS OF AROCLOR 1242 IN HYDRAULIC FLUID

Statistical Parameter	HECD		ECD	
Low Youden Pair	4	3	4	3
Number of Data Points	15	15	16	16
True Value, mg/kg	39.80	47.10	39.80	47.10
Mean Recovery, mg/kg	34.43	32.91	31.94	33.03
Accuracy As % Rel Error	-13.08	-30.13	-19.76	-29.87
Overall Std Dev (S), mg/kg	6.78	6.31	8.90	9.17
Overall Rel Std Dev, %	19.70	19.18	27.86	27.76
Single Std Dev, (SR), mg/kg	5.60		2.46	
Analyst Rel Dev, %	16.62		7.58	
Medium Youden Pair	5	2	5	2
Number of Data Points	15	15	16	15
True Value, mg/kg	64.30	95.70	64.30	95.70
Mean Recovery, mg/kg	54.57	76.13	59.38	79.97
Accuracy As % Rel Error	-15.13	-20.45	-7.65	-16.43
Overall Std Dev (S), mg/kg	7.46	15.81	17.20	14.86
Overall Rel Std Dev, %	13.67	20.77	28.96	18.58
Single Std Dev, (SR), mg/kg	10.57		10.16	
Analyst Rel Dev, %	16.17		14.59	
High Youden Pair	6	1	6	1
Number of Data Points	15	15	15	15
True Value, mg/kg	402.00	492.00	402.00	492.00
Mean Recovery, mg/kg	360.67	441.60	354.13	453.33
Accuracy As % Rel Error	-10.28	-10.24	-11.91	-7.86
Overall Std Dev (S), mg/kg	39.31	55.92	45.18	56.04
Overall Rel Std Dev, %	10.90	12.66	12.76	12.36
Single Std Dev, (SR), mg/kg	30.10		35.57	
Analyst Rel Dev, %	7.50		8.81	

TABLE 9. STATISTICAL SUMMARY OF ANALYSIS OF 2-MCB IN HYDRAULIC FLUID

Statistical Parameter	HECD		ECD	
Low Youden Pair	4	3	4	3
Number of Data Points	12	14	16	16
True Value, mg/kg	41.30	55.60	41.30	55.60
Mean Recovery, mg/kg	30.71	34.66	34.42	37.59
Accuracy As % Rel Error	-25.65	-37.65	-16.66	-32.40
Overall Std Dev (S), mg/kg	3.41	11.39	16.25	11.21
Overall Rel Std Dev, %	11.12	32.84	47.21	29.82
Single Std Dev, (SR), mg/kg	3.75		9.06	
Analyst Rel Dev, %	11.46		25.18	
Medium Youden Pair	5	2	5	2
Number of Data Points	13	14	16	16
True Value, mg/kg	350.00	438.00	350.00	438.00
Mean Recovery, mg/kg	313.54	399.57	255.88	387.75
Accuracy As % Rel Error	-10.42	-8.77	-26.89	-11.47
Overall Std Dev (S), mg/kg	44.09	112.85	90.88	125.07
Overall Rel Std Dev, %	14.06	28.24	35.52	32.26
Single Std Dev, (SR), mg/kg	78.23		92.43	
Analyst Rel Dev, %	21.94		28.72	
High Youden Pair	6	1	6	1
Number of Data Points	14	13	15	16
True Value, mg/kg	847.00	1018.00	847.00	1018.00
Mean Recovery, mg/kg	864.43	1004.31	778.20	970.81
Accuracy As % Rel Error	2.06	-1.35	-8.12	-4.64
Overall Std Dev (S), mg/kg	88.90	122.52	193.99	380.96
Overall Rel Std Dev, %	10.28	12.20	24.93	39.24
Single Std Dev, (SR), mg/kg	45.04		165.91	
Analyst Rel Dev, %	4.82		18.97	

TABLE 10. STATISTICAL SUMMARY OF ANALYSIS OF AROCLOR 1254 IN TRANSFORMER OIL

Statistical Parameter	HECD		ECD	
Low Youden Pair	6	3	6	3
Number of Data Points	16	16	16	14
True Value, mg/kg	32.50	38.70	32.50	38.70
Mean Recovery, mg/kg	28.74	39.54	28.02	36.44
Accuracy As % Rel Error	-11.58	2.16	-13.79	-5.83
Overall Std Dev (S), mg/kg	10.61	11.80	6.33	4.28
Overall Rel Std Dev, %	36.91	29.84	22.61	11.74
Single Analyst Std Dev, (SR), mg/kg	7.06		3.12	
Single Analyst Rel Dev, %	20.69		9.68	
Medium Youden Pair	2	5	2	5
Number of Data Points	16	16	15	15
True Value, mg/kg	68.50	80.70	68.50	80.70
Mean Recovery, mg/kg	65.12	81.83	68.88	81.09
Accuracy As % Rel Error	-4.94	1.40	0.55	0.48
Overall Std Dev (S), mg/kg	14.87	19.66	7.97	10.37
Overall Rel Std Dev, %	22.84	24.03	11.57	12.79
Single Analyst Std Dev, (SR), mg/kg	11.66		6.02	
Single Analyst Rel Dev, %	15.87		8.03	
High Youden Pair	1	4	1	4
Number of Data Points	16	14	16	14
True Value, mg/kg	332.00	392.00	332.00	392.00
Mean Recovery, mg/kg	334.25	393.64	342.44	384.86
Accuracy As % Rel Error	0.68	0.42	3.14	-1.82
Overall Std Dev (S), mg/kg	68.77	54.84	54.00	36.37
Overall Rel Std Dev, %	20.57	13.93	15.77	9.45
Single Analyst Std Dev, (SR), mg/kg	41.21		14.69	
Single Analyst Rel Dev, %	15.87		4.04	

TABLE 11. STATISTICAL SUMMARY OF ANALYSIS OF DCB IN TRANSFORMER OIL

Statistical Parameter	HECD		ECD	
Low Youden Pair	6	3	6	3
Number of Data Points	17	17	13	13
True Value, mg/kg	0.37	0.55	0.37	0.55
Mean Recovery, mg/kg	0.45	0.55	0.36	0.57
Accuracy As % Rel Error	22.42	-0.11	-1.39	3.76
Overall Std Dev (S)	0.23	0.22	0.14	0.26
Overall Rel Std Dev, %	51.39	40.05	37.95	45.56
Single Std Dev, (SR), mg/kg	0.14		0.11	
Analyst Rel Dev, %	27.19		23.42	
Medium Youden Pair	5	2	5	2
Number of Data Points	13	16	17	19
True Value, mg/kg	5.71	3.86	5.71	3.86
Mean Recovery, mg/kg	5.82	8.79	5.41	7.95
Accuracy As % Rel Error	1.89	127.82	-5.31	105.97
Overall Std Dev (S), mg/kg	2.06	9.58	2.00	8.75
Overall Rel Std Dev, %	35.41	108.93	36.95	110.03
Single Std Dev, (SR), mg/kg	0.79		4.40	
Analyst Rel Dev, %	10.78		65.91	
High Youden Pair	1	4	1	4
Number of Data Points	16	14	17	16
True Value, mg/kg	11.20	16.60	11.20	16.60
Mean Recovery, mg/kg	24.47	17.60	11.26	16.96
Accuracy As % Rel Error	118.47	6.02	0.53	2.15
Overall Std Dev (S), mg/kg	27.14	6.40	4.07	5.81
Overall Rel Std Dev, %	110.93	36.34	36.11	34.25
Single Std Dev, (SR), mg/kg	2.90		1.66	
Analyst Rel Dev, %	13.78		11.77	

TABLE 12. STATISTICAL SUMMARY OF ANALYSIS OF AROCLOR 1254 IN WASTE OIL

Statistical Parameter	HECD		ECD	
Low Youden Pair	3	6	3	6
Number of Data Points	16	17	17	17
True Value, mg/kg	38.60	46.90	38.60	46.90
Mean Recovery, mg/kg	33.10	35.90	30.54	36.99
Accuracy As % Rel Error	-14.25	-23.45	-20.88	-21.13
Overall Std Dev (S), mg/kg	9.96	12.27	6.62	6.97
Overall Rel Std Dev, %	30.09	34.17	21.66	18.84
Single Std Dev, (SR), mg/kg	6.93		4.52	
Analyst Rel Dev, %	20.09		13.38	
Medium Youden Pair	2	4	2	4
Number of Data Points	17	17	16	17
True Value, mg/kg	56.10	71.70	56.10	71.70
Mean Recovery, mg/kg	43.91	52.72	45.19	59.45
Accuracy As % Rel Error	-21.73	-26.47	-19.45	-17.08
Overall Std Dev (S), mg/kg	13.01	20.77	9.63	13.26
Overall Rel Std Dev, %	29.63	30.40	21.31	22.27
Single Std Dev, (SR), mg/kg	13.61		7.69	
Analyst Rel Dev, %	28.17		14.69	
High Youden Pair	1	5	1	5
Number of Data Points	16	15	15	17
True Value, mg/kg	350.00	461.00	350.00	461.00
Mean Recovery, mg/kg	286.44	412.20	330.53	429.29
Accuracy As % Rel Error	-18.16	-10.59	-5.56	-6.88
Overall Std Dev (S), mg/kg	64.70	43.77	46.15	42.30
Overall Rel Std Dev, %	22.59	10.62	13.96	9.85
Single Std Dev, (SR), mg/kg	28.80		31.44	
Analyst Rel Dev, %	8.24		8.28	

ACCURACY AND PRECISION STATEMENTS

The regression equations for accuracy and precision are listed in Table 1 and provide a measure of expected performance for the routine analysis of PCB's in oil using the HECD and ECD methods.

TSCA regulations have been promulgated for the disposal of controlled waste containing PCB's in concentrations between the limit of quantitation

and 50 mg/kg and greater than 50 mg/kg. A comparison at the HECD and ECD methods at a concentration level of 50 mg/kg for each of the PCB's and Oils is shown for percent recovery, overall standard deviation, and single-analyst standard deviation in Tables 13, 14 and 15, respectively. The respective values were obtained from the regression equations in Table 1. DCB has been excluded from the Tables since the concentration ranged studied was from 0.37-17 mg/kg.

TABLE 13. PERCENT RECOVERY FOR HECD AND ECD METHODS AT 50 mg/kg

MATRIX	COMPOUND	HECD	ECD
Capacitor Fluid	Aroclor 1016	88.4	87.2
Hydraulic Fluid	Aroclor 1242	80.4	80.2
	2-MCB	71.0	77.4
Transformer Oil	Aroclor 1260	96.8	95.0
Waste Oil	Aroclor 1254	80.0	81.0
		83.3%	84.2%

TABLE 14. OVERALL STANDARD DEVIATION, mg/kg AT 50 mg/kg

MATRIX	COMPOUND	HECD	ECD
Capacitor Fluid	Aroclor 1016	11.1	12.6
Hydraulic Fluid	Aroclor 1242	7.4	10.7
	2-MCB	7.4	14.8
Transformer Oil	Aroclor 1260	13.2	7.4
Waste Oil	Aroclor 1254	13.1	8.2
	Mean	10.4	10.7

TABLE 15. SINGLE-ANALYST STANDARD DEVIATION, mg/kg AT 50 mg/kg

MATRIX	COMPOUND	HECD	ECD
Capacitor Fluid	Aroclor 1016	9.0	8.6
Hydraulic Fluid	Aroclor 1242	6.5	3.7
	2-MCB	4.2	10.6
Transformer Oil	Aroclor 1260	8.8	3.8
Waste Oil	Aroclor 1254	9.2	5.7
	Mean	7.5	6.4

Generally, there is good agreement between the two methods. The mean recoveries for all PCB's in the four oils were 83.3 percent using HECD compared to 84.2% using ECD. The mean overall precision for the PCB's in the four oils for HECD were 10.4 as compared to 10.7 for ECD and the mean single-analyst precision was 7.5 for HECD as compared to 6.4 for ECD. However, the mean percent recovery for HECD appears low since the method requires only sample dilution. The ECD mean recovery is reasonable considering the variety of sample preparation procedures and its quenching effect upon the ECD.

The slopes of the regression equations for DCB in transformer oil for HECD and ECD are 1.63 and 1.26, respectively. Since the magnitude of the regression intercepts are relatively small compared to the slopes, a rough comparison of percentage recovery for these methods can be made using these slopes. As such, the mean DCB recoveries are high for both methods, and may be due to poor integration of the late-eluting broad peak. If the GC oven temperature is too low the DCB elutes as a broad band whose terminus may be hard to define for integration. The ECD method provides a more accurate recovery because it responds much more strongly to the DCB than does the HECD. The poor precision as indicated by the slopes of the regression equations for S also indicates a problem with the analytical

procedure. Examination of the statistical summaries in Table 11 indicate exceptionally large percent overall relative standard deviations for ampuls one and two for HECD and ampul two for ECD. Further examination of the raw data in Table D-9 and D-10 for these ampuls indicates that four data points in each of the ampuls in question are largely responsible for excessively high recoveries and poor precision, and three out of the four data come from the same laboratories. The outlier test did not reject these data; however, if it had, the following statistics in Table 16 would have been obtained for each of the three questionable data sets.

TABLE 16. NEW STATISTICS FOR DCB

DETECTOR/AMPUL	PERCENT* RECOVERY	OVERALL S (mg/kg)	SINGLE-ANALYST Sr (mg/kg)
HECD			
Ampul one (with data)	218	27.14	2.90
Ampul one (without data)	110	4.3	2.90
Ampul two (with data)	228	9.58	0.79
Ampul two (without data)	96	1.37	0.79
ECD			
Ampul two (with data)	206	8.75	4.40
Ampul two (without data)	103	1.05	0.07

* detained as - the mean concentration devided by the true value times 100 percent.

New regression equations for accuracy, overall precision, and single-analyst, precision without the questionable data are shown in Table 17.

TABLE 17. NEW REGRESSION EQUATIONS

Transformer oil/DCB (0.37-16.6 mg/Kg)

HECD $X = 1.02\ C + 0.05$ $S = 0.39\ X + 0.00$ $SR = 0.12\ X + 0.08$

ECD $X = 1.01\ C + 0.00$ $S = 0.37\ X + 0.03$ $SR = 0.06\ X + 0.08$

It is apparent that the new regression equations are more accurate and precise over the concentration range studied. However, the regression equations shown in Table 1 include these data. It should be pointed out, that the ECD method recoveries without these data points still appear high since the oil should quench the detector to produce results having up to a 20 percent negative bias.

METHOD EVALUATION

The HECD and ECD methods had equivalent recoveries, overall standard deviation, and single-analyst standard deviation when comparing the means for all Aroclors and oil types at 50 mg/kg. However, individual differences appeared to exist. To determine if these differences were of statistical significance, the test previously described under "Comparison of Accuracy and Precision Across Detector Types," Section 4, was applied. The HECD method was used as the base method, and the ECD method was compared to it in terms of recovery and precision. These analyses are summarized in Table 18. In all cases, there is no evidence of a statistically significant effect on accuracy or precision due to detector type since $P(F>FOBS) \geq 0.05$.

TABLE 18. TEST FOR DIFFERENCE BETWEEN DETECTORS

Oil Type and PCB	Observed F-Value	P (F>FOBS)
Capacitor - 1016	1.99	0.14
Hydraulic - 1242	0.02	0.98
Hydraulic - 2 - MCB	1.58	0.21
Transformer - 1260	0.19	0.82
Transformer - DCB	1.11	0.33
Waste Oil - 1254	0.89	0.41

However, the two methods do differ in their method detection limits (MDL). The MDL is defined as the minimum concenration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. It was determined from the replicate analyses of a sample

spiked at one to five times the estimated MDL and was computed from the standard deviation of seven replicate analyses and the Student's t-value (9). The MDL for oils analyzed by the HECD method for Aroclors varied from 3 to 15 mg/kg. The wide variability shows the dependence of the MDL on matrix type and indicates the great effect that sample matrices have on the HECD. On the other hand, the MDL for oils analyzed by the ECD method for Aroclors was 2 mg/kg for all but the waste oil at 4 mg/kg. The ECD detection limit is lower and more precise than the HECD detection limit for the anlaysis of Aroclors. The HECD detection limit is matrix dependent and varies with the oil type.

The chromatographic methods are applicable to a wide range of oils, but each method has its advantages and disadvantages. The HECD method requires minimum sample preparation, diluting the sample in an appropriate solvent according to the USEPA recommended method. However, operational problems, such as coking in the reactor tube and column overloading, can occur. The sole HECD manufacturer (Tracor Inc.) strongly recommends that the PCB's be extracted from the oil sample with methanol to prevent injecting oil on the GC column or that the oven temperature be programmed to elute the oil before the PCB's. Although interferences do not appear in the PCB chromatogram, sample pretreatment may provide more accurate and precise analysis and may extend the life of the GC column and HECD.

The ECD is considered by many analysts to be easier to operate, maintain, and troubleshoot than the HECD. However, it requires sample preparation to remove interfering compounds, and the required sample cleanup procedure is matrix dependent.

Both the HECD and ECD methods provide accurate and precise analyses of PCB's in oil. The advantages and limitations of each method should be considered when using these methods.

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APPENDIX A

1. White, L.D. et al., AIHA Journal, 31, 225 (1970).

APPENDIX A PERFORMANCE EVALUATION INSTRUCTIONS

June 4, 1981

TO: PCB ROUND ROBIN SUBCONTRACTORS

Enclosed you will find the instructions and answer sheet for your performance evaluation for the determination of PCBs in oil. Two samples (a waste oil and a hydraulic fluid) are being sent under separate cover and are to be analyzed by both the electron capture detection (ECD) method and the electrolytic conductivity detection (HECD) method. PCB standards are being sent by EPA from their repository at Radian. Monochlorobiphenyl and decachlorobiphenyl standards can be obtained from RFR or RTP.

Satisfactory performance must be attained in order to participate in this study. Satisfactory performance is defined as determining sample concentrations which are within 20% of the spiked concentration and which pass the outlier test. All directions must be followed precisely. If you have any questions or need clarification, please call Versar immediately. A quick question may save time and effort on your part and help others as well.

Unlike other EPA method validations, there will be no prestudy conference. Therefore, it is imperative that any questions, comments, or suggestions be expressed during the performance evaluation. The purpose of this validation study is to measure the precision and accuracy of the PCB method as written. No variations or substitutions can be made in the final instructions. Any comments arising from the performance evaluation will be addressed and incorporated into the final instructions as appropriate.

Results, chromatograms, and calculations are due to Versar by June 29, 1981. Calculations should be based upon as many peaks as possible, and those peaks should be indicated on the chromatograms. Also indicate the oven temperature on the chromatograms and under "Comments".

Sincerely yours,

Susan Nohr

Susan Nohr, Ph.D.
Contract Manager

SN:mjk

Enclosure

APPENDIX A PERFORMANCE EVALUATION INSTRUCTIONS (Cont.)

Answer Sheet

Determination of PCBs in Oil

1) Results From _____(Laboratory) _____(Principal Analyst)

Sample	Vial Number	Aroclor	Spike Level	BCD conc (mg/kg)		HBCD conc (mg/kg)		Recovery (%)		Precision (Rel % Diff)
				by area	by pk. ht.	by area	by pk. ht.	BCD	HBCD	
Hydraulic			NA					NA	NA	NA
Waste Oil			NA					NA	NA	NA
Spiked Sample										NA
Method Standard	NA									
Duplicate Method Standard	NA									

2) Attach identified chromatograms and sample calculations.

3) List any divergence from the method.

4) Comment, question, or suggest modifications.

APPENDIX B

METHOD STUDY INSTRUCTIONS AND METHODOLOGY

THE ANALYSIS OF POLYCHLORINATED BIPHENYLS IN
TRANSFORMER FLUID, CAPACITOR FLUID, HYDRAULIC FLUID, AND WASTE OIL

Validation Instructions

1. Scope

1.1 This is a round robin study to validate the following method for PCB analysis. Since the analytical parameters and equipment design will affect the validity of the analytical results, all such parameters and designs are to be used as specified. Anyone needing to deviate from the method must contact the Project Manager (Dr. Susan Sonchik) at Versar before doing so.

1.2 This is a gas chromatographic (GC) method applicable to the determination of commercial mixtures of polychlorinated biphenyls (PCB's) in transformer oils, capacitor fluids, hydraulic fluids, and certain other hydrocarbon-based waste oils.

1.3 The detection limits are dependent upon the complexity of the sample matrix and the ability of the analyst to properly maintain the analytical system. Using a carefully optimized instrument, this method has been shown to be useful for the determination of commercial PCB mixtures spiked into transformer fluid over a range of 5.0 to 500 mg/kg. Based upon a statistical calculation at 5 mg/kg for a simple oil matrix, the method detection limit for Aroclors 1016, 1221, 1242, 1254, and 1260 is 1 mg/kg by ECD and 20 mg/kg by HECD. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be

measured and reported with 99% confidence that the value is above zero.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms.

2. Summary

2.1 The sample is diluted on a weight/volume basis so that the concentration of each PCB compound is within the linear range of the GC system (0.02 to 5 ng/µℓ for ECD and 1 to 20 ng/µℓ for HECD).

2.2 The diluted sample is then injected into a gas chromatograph for separation of the PCB compounds. Measurement is accomplished with a halogen-specific detector (HECD), which maximizes baseline stability and minimizes interferences normally encountered with other detectors, and with an electron capture detector (ECD). Several cleanup techniques are required for samples analyzed by ECD.

2.3 The concentrations of the PCB's are calculated on a mg/kg basis, using commercial mixtures of PCB's as standards.

3. Apparatus

3.1 Gas Chromatograph - The gas chromatograph should be capable of accepting 1/4-inch OD glass columns and equipped for on-column injection.

3.2 Gas Chromatographic Detector

3.2.1 A halogen specific detector (the electrolytic conductivity detector) is used to eliminate interferences causing misidentifications or false-positive values due to non-organohalides which commonly co-elute with the PCB's.

3.2.2 A semi-specific detector (the electron capture detector) can be used when sample chromatographic patterns closely match those of the standards. Sample cleanup is required when the ECD is used.

3.3 Gas Chromatographic Columns

3.3.1 The GC column and conditions listed below are required for the validation of the analysis of PCB mixtures in oil. The analyst may vary the column temperature and flow ONLY to improve separation. The PCB's must be adequately resolved in the various Aroclor mixtures so that each Aroclor is identifiable through pattern recognition. (See Figures 1 through 12 to establish this.)

3.3.2 Analytical Column - Glass, 1/4 in. OD (2mm ID) 6 ft. (180 cm) long, packed with Gas Chrom Q 100/120 mesh coated with 3% OV-1.

Carrier Gas - 20 to 60 mℓ/min (helium, nitrogen, 5% or 10% methane in argon).

Isothermal Operation - Monochlorobiphenyl, 140° to 200°C; Aroclors 1016, 1241, 1254, 1260, and decachlorobiphenyl, 170° to 250°C.

3.4 Volumetric Flasks - 10, 25, 100, 200, and 250 mℓ.

3.5 Pipets - 0.10, 1.0, and 5.0 mℓ Mohr delivery, disposable transfer, or Pasteur.

3.6 Micro Syringes - 10.0 µℓ.

3.7 Sample Containers - 20 mℓ or larger screw cap bottles with Teflon-faced cap liners. (Aluminum foil cap liners can be used.)

3.8 Chromatographic Column - Chromaflex, 500 mm long x 19 mm ID (kontes K-420540-9011 or equivalent).

4. Reagents and Materials

4.1 Reagent Safety Precautions

4.1.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard.

From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.1.2 PCB's have been tentatively classified as known or suspected, human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood.

4.2 Hexane (mixed hexanes), iso-octane, of pesticide grade.

4.3 Recommended Column Packing - Gas Chrom Q 100/120 mesh coated with 3% OV-1.

4.4 Standards

4.4.1 Aroclors 1016, 1242, 1254, 1260. Primary dilutions of various Aroclors in iso-octane will be available from U.S. EPA, EMSL, Cincinnati Quality Assurance Branch, 26 W. St. Clair Street, Cincinnati, Ohio 45268 (Attention: Mr. Harry Kolde).

4.4.2 2-chlorobiphenyl and decachlorobiphenyl (available from Ultra-Scientific Inc. or RTP).

4.4.3 Alumina (Fisher A540 or equivalent).

4.4.4 Florisil (PR grade or equivalent).

4.4.5 Sulfuric acid ACS.

4.5 Standard Stock Solutions - Primary dilutions of each of the Aroclors or individual PCB's should be obtained from EPA. Store the primary dilutions at 4°C in 10 to 15 mℓ narrow-mouth, screw cap bottles with Teflon-cap liners. Primary dilutions are stable indefinitely if the seals are maintained. The validity of primary and secondary dilutions must be monitored on a quarterly basis by analyzing EMSL/CI Quality Control Check Samples.

4.6 Working Standards - Prepare working standards similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Dilute the mixture to volume with pesticide-grade hexane. Calculate the concentration in ng/µℓ as the individual PCB's. Store dilutions at 4°C in 10 to 15 mℓ narrow-mouth, screw cap bottles with Teflon-cap liners. If the seals are maintained, these secondary dilutions can be stored indefinitely.

4.7 PCB Locator Mixture - Prepare a PCB locator mixture containing 0.1 µg/mℓ of 2-chlorobiphenyl, 0.5 µg/mℓ Aroclor 1242, 0.5 µg/mℓ Aroclor 1260, and 0.1 µg/mℓ of decachlorobiphenyl in hexane. Use the chromatogram generated by the PCB locator mixture to help identify the retention times of the various PCB isomers commonly found in commercial PCB mixtures. (This mixture is equivalent to 100 ppm MCB and DCB and 50 ppm Aroclors. Aroclors 1242 and 1260 can be detected by ECD and HECD. The MCB and DCB may need to be fortified for the ECD and HECD, respectively.)

5. Procedure

5.1 For samples to be analyzed by the HECD Method, dilute the oil at the rate 25:1 in hexane.

5.1.1 Weigh approximately 1 gram to ± 0.001 gram of sample in a 25 mℓ volumetric flask and dilute to 25 mℓ with hexane. Stopper and mix.

5.1.2 Analyze the diluted sample according to Section 5.4 or store the diluted sample in a narrow-mouth bottle with a Teflon-lined screw cap.

5.2 For samples outside the linear range of the detector, dilute at a rate of 250:1 in hexane.

5.2.1 Weigh approximately 0.1 gram to ± 0.001 gram of sample in a 25 mℓ volumetric flask and dilute to volume with hexane. Stopper and mix.

5.2.2 Analyze the diluted sample according to Section 5.4 or store the diluted sample in a narrow-mouth bottle with a Teflon-lined screw cap.

5.2.3 If the concentration of PCB's is still too high for the chromatographic system, prepare secondary dilutions from Section 5.2.1 until acceptable levels are obtained.

5.3 For samples to be analyzed by the ECD method, the oil must be cleaned prior to injection.

5.3.1 For the Validation Study, each oil type is spiked with the following Aroclors and should be prepared for ECD analysis according to the indicated procedures:

Transformer Oil	1260 and DCB	Section 6.1
Waste Oil	1254	Section 6.2
Hydraulic Fluid	1242 and 2-MCB	Section 6.3
Capacitor Fluid	1016	Section 6.3

5.3.2 For sulfuric acid cleanup, the sample must be diluted at a rate of 100:1 in hexane before acid treatment. Dilute according to 5.1.1 using 100 mℓ hexane instead of 25 mℓ.

5.4 Analyze the sample by injecting the hexane mixture into the gas chromatograph using auto injectors or the solvent flush technique.[1]

5.4.1 When the ECD is used, cleanup techniques must be performed prior to injection and will incorporate the necessary dilution.

5.4.2 Recommended injection volumes: HECD, 3 to 5 µℓ; ECD, 2 to 3 µℓ. Smaller volumes may be injected when auto injectors are used if the resulting method detection limits are acceptable.

5.5 If the resulting chromatogram shows evidence of column flooding or non-linear responses due to excess sample, further dilute the sample according to Section 5.2.3

5.6 Determine whether or not PCB's are present in the sample by comparing the sample chromatogram to that of the PCB locator mixture (Section 4.7).

5.6.1 If a series of peaks in the sample match some of the retention times of PCB's in the PCB locator mixture, attempt to identify the source by comparing chromatograms of each standard prepared from commercial mixtures of PCB's (see Section 4.6). Proceed to Section 9.4 if the source of PCB's is identified.

5.6.2 If a sample with a dilution ratio of 1000:1 or higher was analyzed and no measurable PCB peaks were detected, analyze an aliquot of sample diluted to 100:1.

---

[1] White, L.D. et.al., AIHA Journal, 31, 225 (1970).

6. Cleanup

Several tested cleanup techniques are described. Depending upon the type of oil, use the indicated cleanup procedure which is required to resolve the PCB's from interferences.

6.1 Acid Cleanup (use for Transformer Oils)

6.1.1 Place 5.0 mℓ of concentrated sulfuric acid into a 40 mℓ narrow-mouth screw cap bottle. Add 10.0 mℓ of the diluted sample. Seal the bottle with a Teflon-lined screw cap and shake for 1 minute.

6.1.2 Allow the phases to separate, transfer the sample (upper phase) to a clean narrow-mouth screw cap bottle. Seal with a Teflon-lined cap.

6.1.3 Analyze according to Section 5.4

6.1.4 If the sample is highly contaminated, a second or third acid cleanup may be employed.

NOTE: This cleanup technique was tested over a period of about 6 months using both electron capture and electrolytic conductivity detectors. Care was taken to exclude any samples that formed an emulsion with the acid. The sample was withdrawn well above the sample-acid interface. Under these conditions, no adverse effects associated with column performance and detector sensitivity to PCB's were noted. This cleanup technique could adversely affect the chromatographic column performance for future acid degradable samples.

6.2 Florisil Column Cleanup (use for Waste Oils)

6.2.1 Variances between batches of Florisil may affect the elution volume of the various PCB's. For this reason, the volume of solvent required to completely elute all of the PCB's must be verified by the analyst. Using an appropriate PCB standard, demonstrate that all PCB's elute

in the 200 mℓ fraction. If not, the weight of Florisil must be adjusted accordingly.

6.2.2 Place a 20.0 gram charge of Florisil, activated at 130°C, into a chromaflex column. (Slurry packing produces less channels than dry packing.) Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70 to 80 mℓ of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

6.2.3 Add 2.0 mℓ of the <u>undiluted</u> sample (weighed accurately to ± 0.001 gram) to the column. Allow the sample to enter the column and carefully wash down the inner wall of the column with a small amount of the hexane. Add 225 mℓ of hexane to the column. Collect and discard the first 25.0 mℓ.

6.2.4 Collect exactly 200 mℓ of hexane eluate in a 200 mℓ volumetric flask. All the PCB's must be in this fraction. No oil should elute in this fraction.

6.2.5 Analyze the sample according to Section 5.4

6.3 <u>Alumina Column Cleanup</u> (use for Capacitor Fluids and Hydraulic Fluids)

6.3.1 Adjust the activity of the alumina by heating to 200°C for 2 to 4 hours. When cool, add 3% water (weight:weight) and mix until uniform. Store in a tightly sealed bottle. Allow the deactivated alumina to equilibrate at least 30 minutes before use. Reactivate weekly.

6.3.2 Variances between batches of alumina may affect the elution volume of the various PCB's. For this reason, the volume of solvent required to completely elute all of the PCB's must be verified by the analyst. Using an

appropriate PCB standard, demonstrate that all PCB's elute in the 250 mℓ fraction. If not, the weight of alumina must then be adjusted according. (If problems persist, the activity of the alumina or the polarity of the solvent may require adjusting.)

6.3.3 Place a 50.0 gram charge of alumina into a Chromaflex column. Slurry packing produces less channels than dry packing and is recommended. Settle the alumina by tapping. Add about 1 cm of anhydrous sodium sulfate. Pre-elute the column with 70 to 80 mℓ of hexane. Just before exposing the sodium sulfate layer to air, stop the flow. Discard the eluate.

6.3.4 Add 2.5 mℓ of the undiluted sample to the column with a 5 mℓ Mohr pipet. Accurately weigh the sample to 0.001 gram by weighing the pipet before and after delivery. Add 300 mℓ of hexane to the column. Carefully wash down the inner walls of the column with a small volume of hexane prior to adding the total volume. Collect and discard the 0 to 50 mℓ fraction.

6.3.5 Collect exactly 250 mℓ of the hexane in a 250 mℓ volumetric flask. All the PCB's must be in this fraction. No oil should elute in the fraction.

6.3.6 Analyze the sample according to Section 5.4.

7. Calibration

Prepare a calibration curve for each Aroclor or PCB detected in the sample. The standard curve must contain at least 3 points, two of which must bracked the sample concentration. When using an electrolytic conductivity detector, if the sample response is in a low-level non-linear area of the calibration curve, two of the calibration points must be checked daily. If the calibration curve is

not within 15 percent of the Quality Check Standard (Reference Standard), recalibrate the instrument.

8. Quality Assurance and Control

Each laboratory participating in this method validation is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of method standards as a continuing check on performance.

8.1 Reagent Blank - Before processing any samples, the analyst must demonstrate that all glassware and reagents are free of interferences. With each batch of samples, a laboratory reagent blank should be processed as a safeguard against undetected contamination.

8.2 Method Standard - Check standards must be prepared and analyzed with each batch of samples to check the accuracy of the method, under optimum conditions, excluding any chemical interference from the sample matrix. The method standard must be processed exactly as the samples, including the cleanup procedures. Report concentration found and the percent recovery.

8.3 Duplicate Method Standard - The check standard must be analyzed in duplicate with each batch of samples to measure the precision of the analysis. The relative percent difference between duplicates $\frac{200\ (X - Y)}{X + Y}$ should be <10%.

8.4 Reference Standard - The calibration curve must be checked daily using a quality control check sample or a reference standard. If agreement between the daily calibration standard and calibration curve are not within $\pm$ 15%, a new calibration curve must be made.

9. Calculations

9.1 Locate each PCB in the sample chromatogram by comparing the retention time of the suspect peak to the retention data gathered from analyzing standards and interference-free Method Standards. The experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.2 If the response for the peak exceeds the working range of the system, dilute according to Section 5.3.3.

9.3 If the measure of the peak response is prevented by the presence of interferences, further cleanup is required.

9.4 If the parent Aroclors or PCB's are identified in the sample, calibrate according to Section 7. The concentration of the PCB's in the sample are calculated by comparing the sum of the responses for all of the PCB's in he standard to the sum of the corresponding PCB's in the sample. This is particularly important as sample concentrations approach within 20 percent of 50 mg/kg or any other EPA regulated concentration. If calculations are based upon a small percentage of the total PCB peaks, serious errors may result. Therefore, all peaks should be used for quantitation. However, minor peaks can be disregarded if (1) interference problems persist after cleanup; or (2) the source of PCB's is obvious. A minimum of 5 (five) peaks must be used for quantitation.

9.4.1 Measure the peak height or peak area of each peak identified as a PCB in Section 9.1 in both the sample and the standard.

9.4.2 Use the following formula to calculate the concentrations of PCB's in the sample:

$$\text{Concentration (mg/kg)} = \frac{B \times V_t}{A \times W}$$

$$A = \frac{\text{Sum of standard peak heights (areas)}}{\text{ng of standard injected}} = \text{mm/ng}$$

$$B = \frac{\text{Sum of sample peak heights (areas)}}{\mu\text{l injected}} = \text{mm/}\mu\text{l}$$

V_t = Dilution volume of sample in ml

W = Weight of the sample in grams

9.4.3 If the calculations are based upon integrated areas, the accuracy of integration must be verified by manual measurement and recalculation based on the peak height of one major peak. If agreement is not within 10%, manual peak height calculation of at least 5 major peaks must be performed.

9.5 Report all data in mg/kg.

9.6 Round off all data to 2 significant figures.

9.7 Report concentration and Aroclor determined. Report monochlorobiphenyl and decachlorobiphenyl separate from the Aroclor concentration.

9.8 Data for the affected parameters of samples processed as part of a batch where the laboratory spiked sample recovery falls outside of the control limits in Section 8.2 must be labeled as suspect.

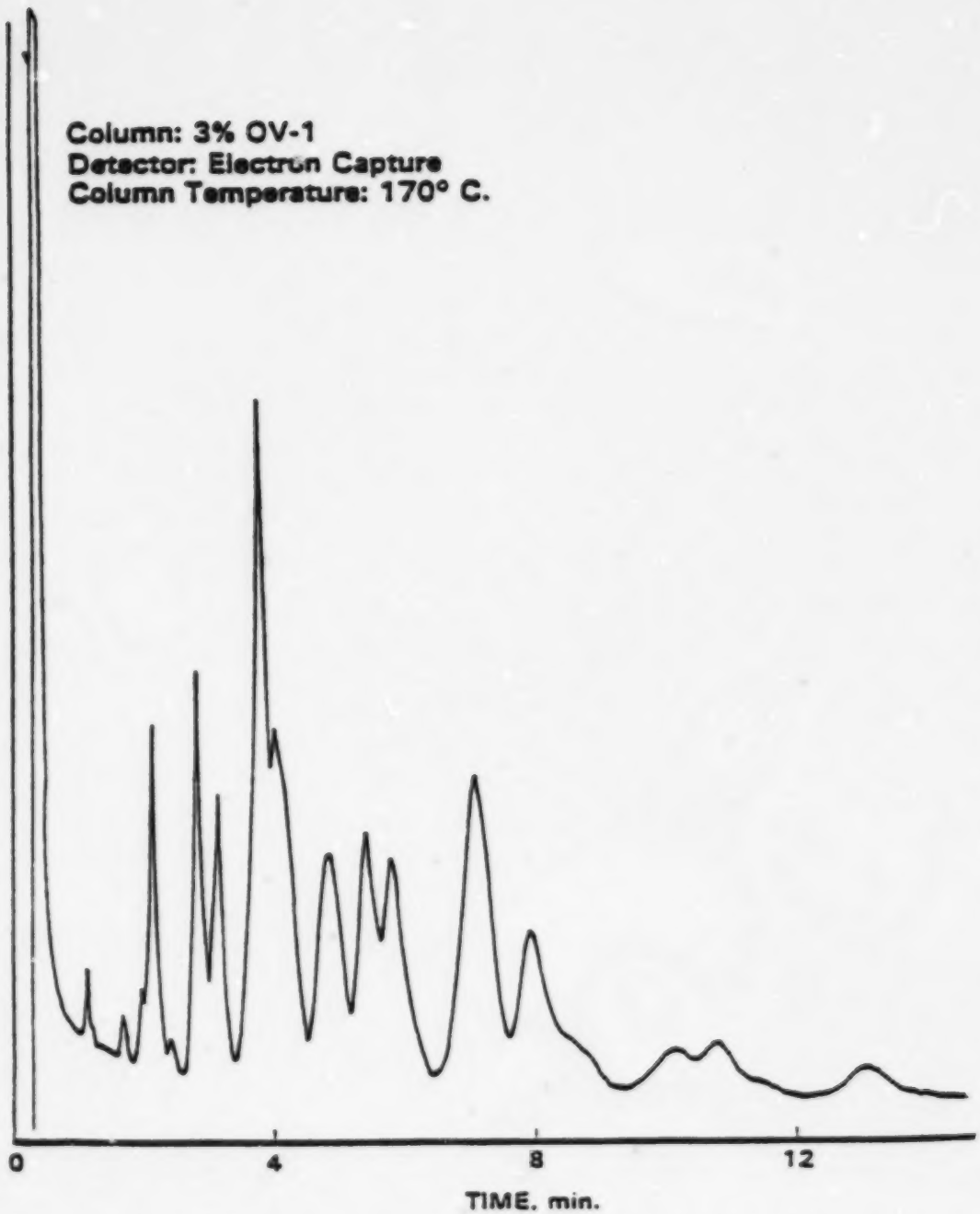


FIGURE B1. GAS CHROMATOGRAM OF AROCLOR 1242

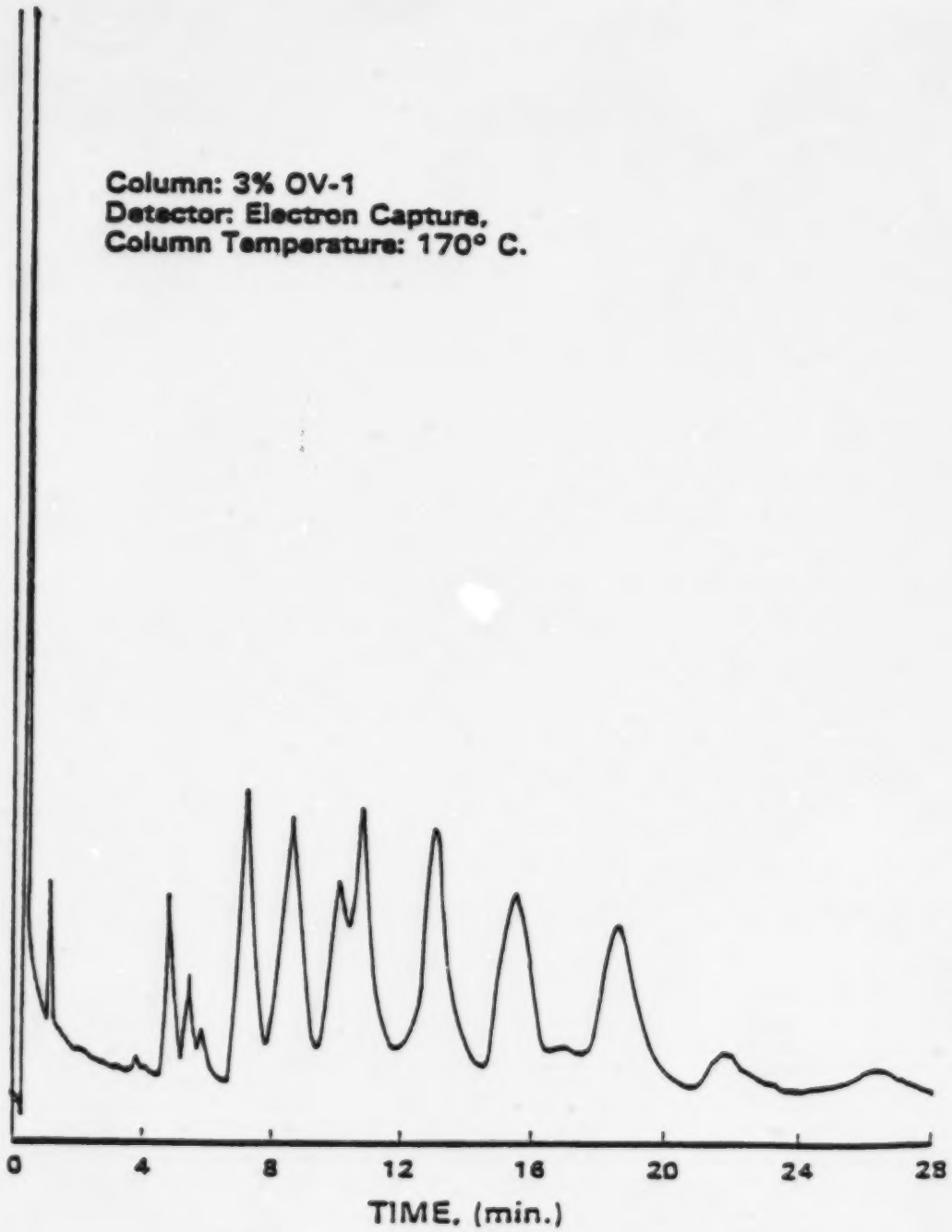


FIGURE B2. GAS CROMATOGRAM OF AROCLOR 1254

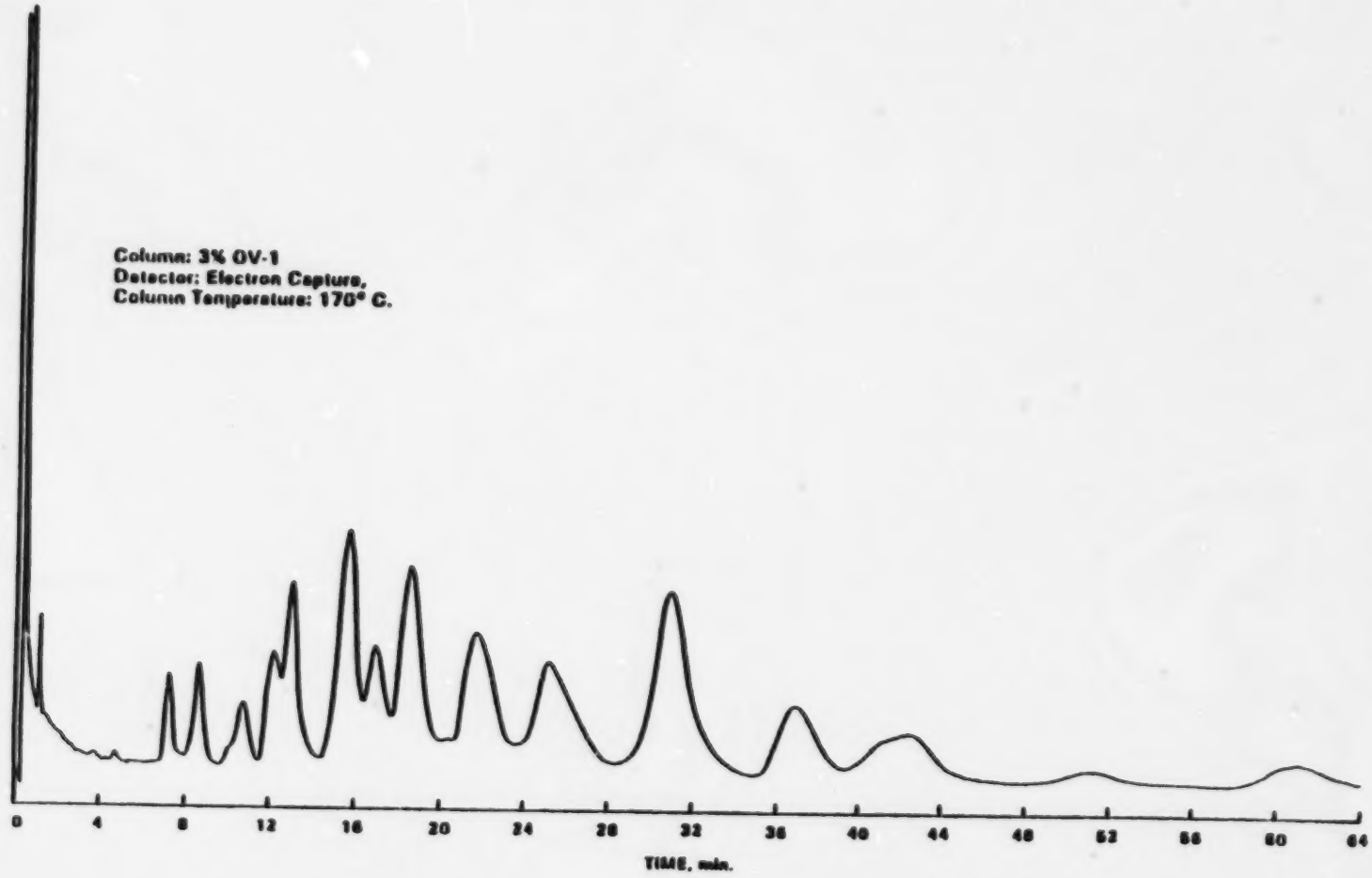


FIGURE B3. GAS CHROMATOGRAM OF AROCLOR 1260

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	190°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

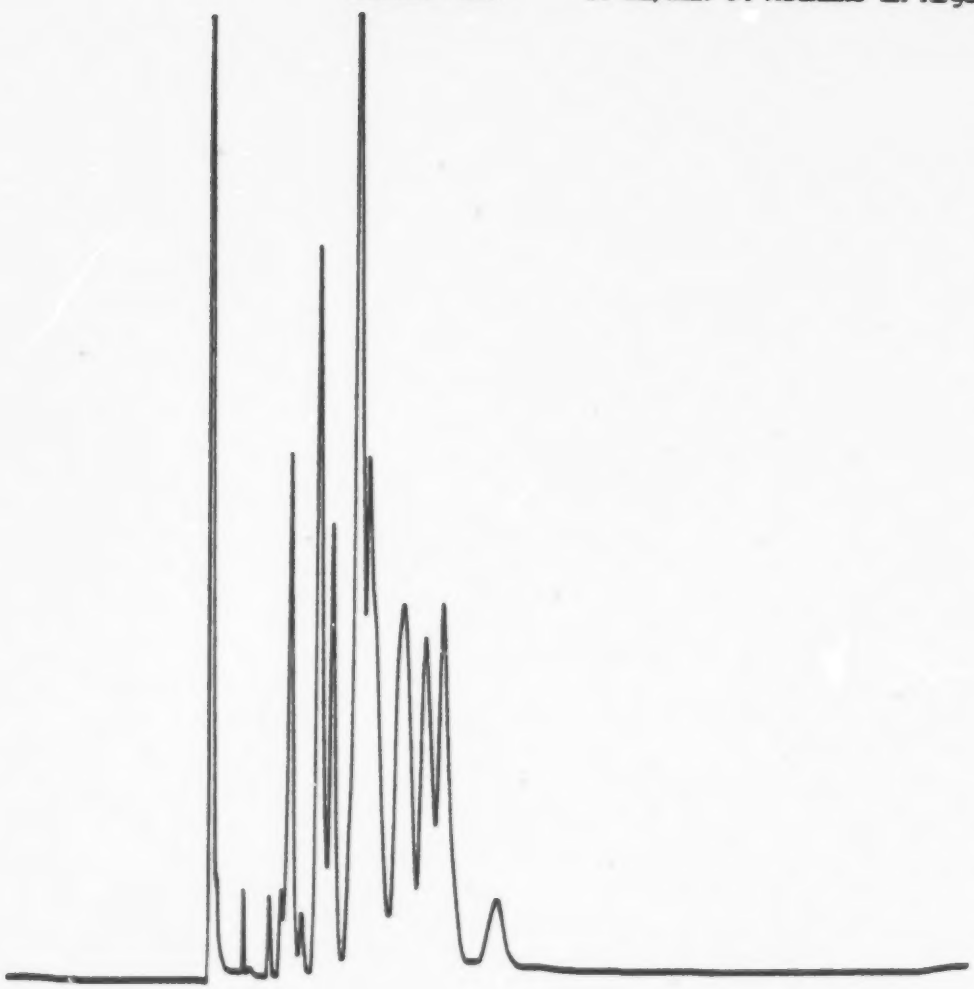


FIGURE B4. AROCLOR 1016 STANDARD CHROMATOGRAM

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	190°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

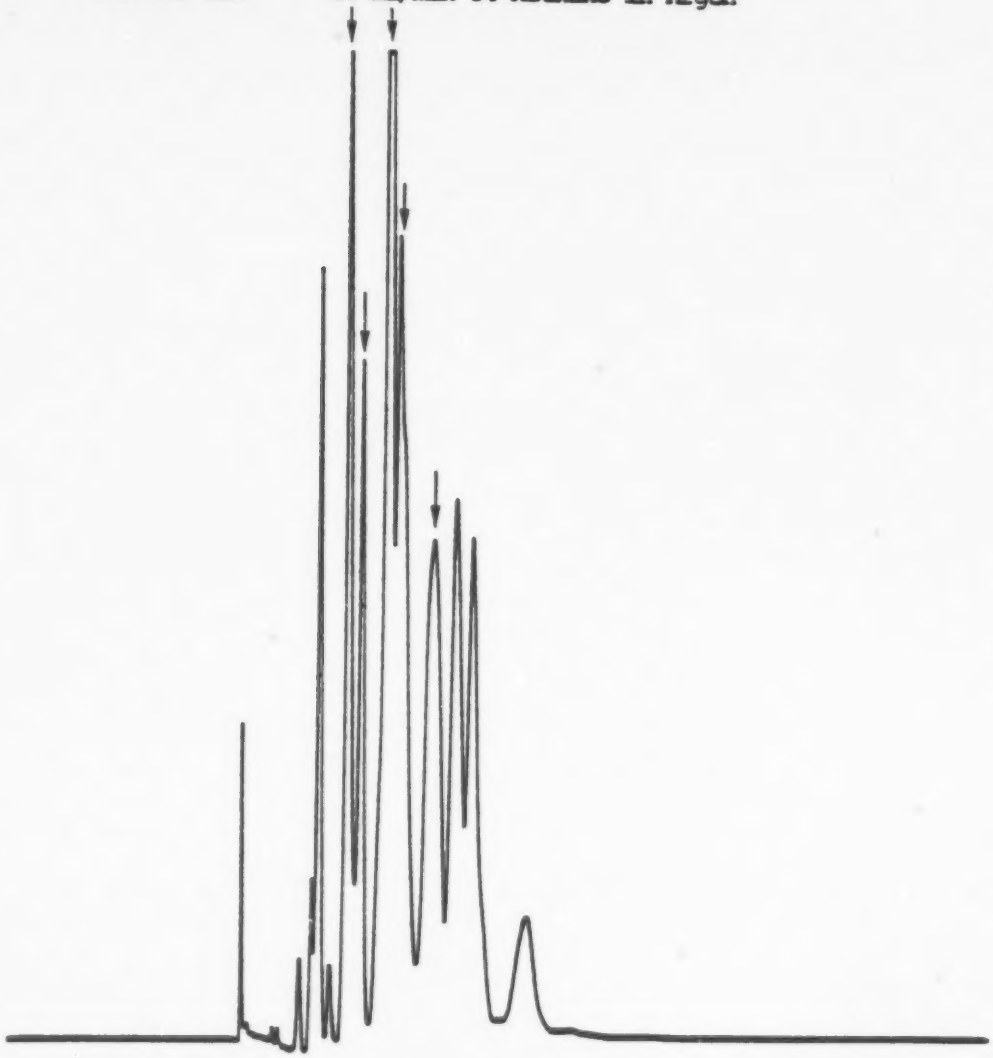


FIGURE B5. CAPACITOR FLUID (Peaks Used For Quantitation)

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	190°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

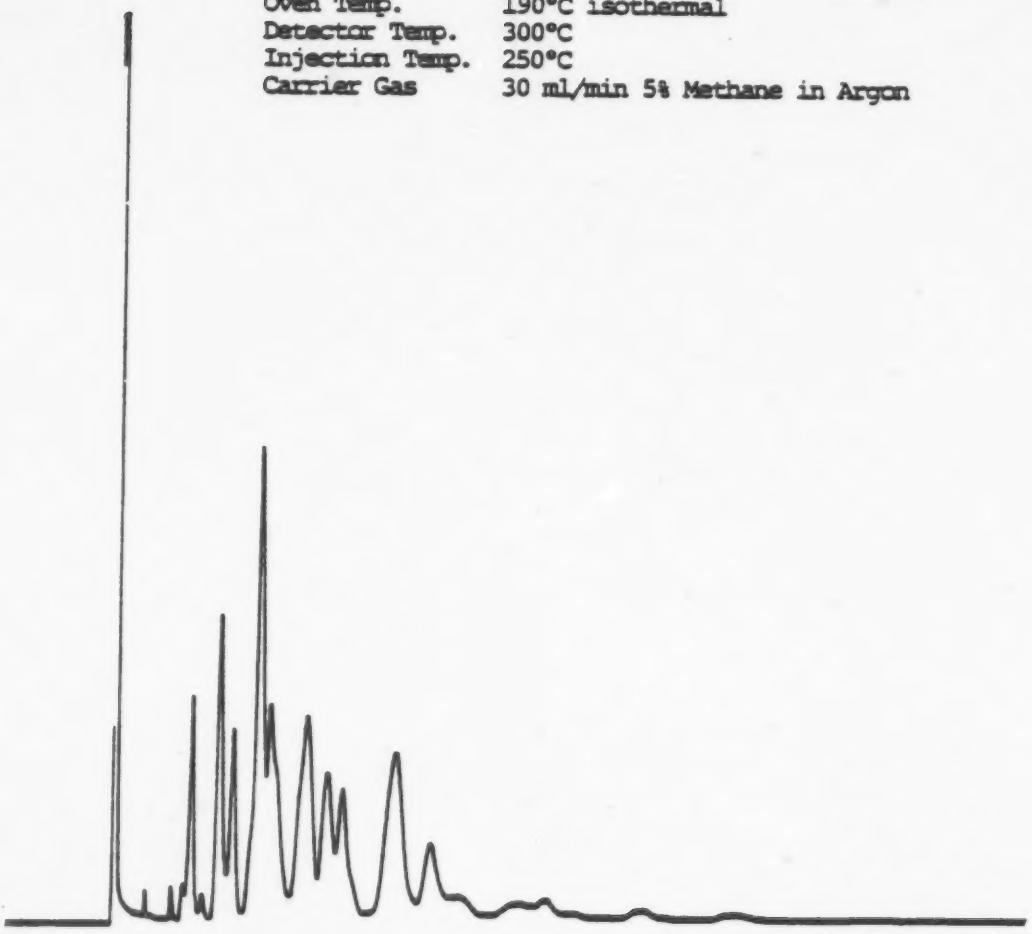


FIGURE B6. AROCLOR 1242 STANDARD CHROMATOGRAM

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	190°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

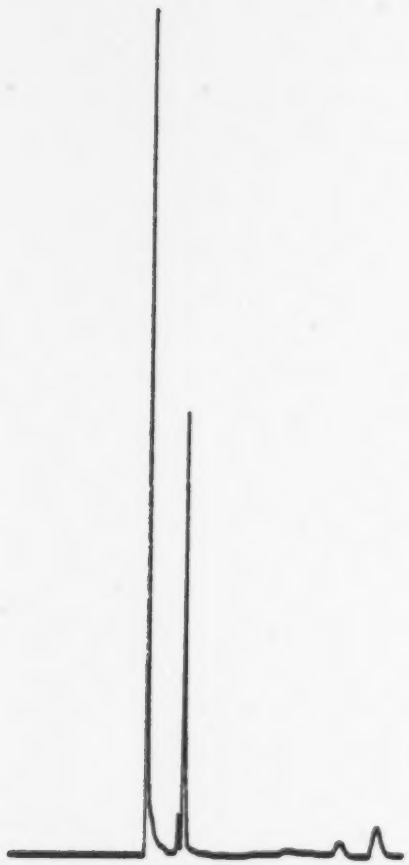


FIGURE B7. 2-MCB STANDARD CHROMATOGRAM

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	190°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

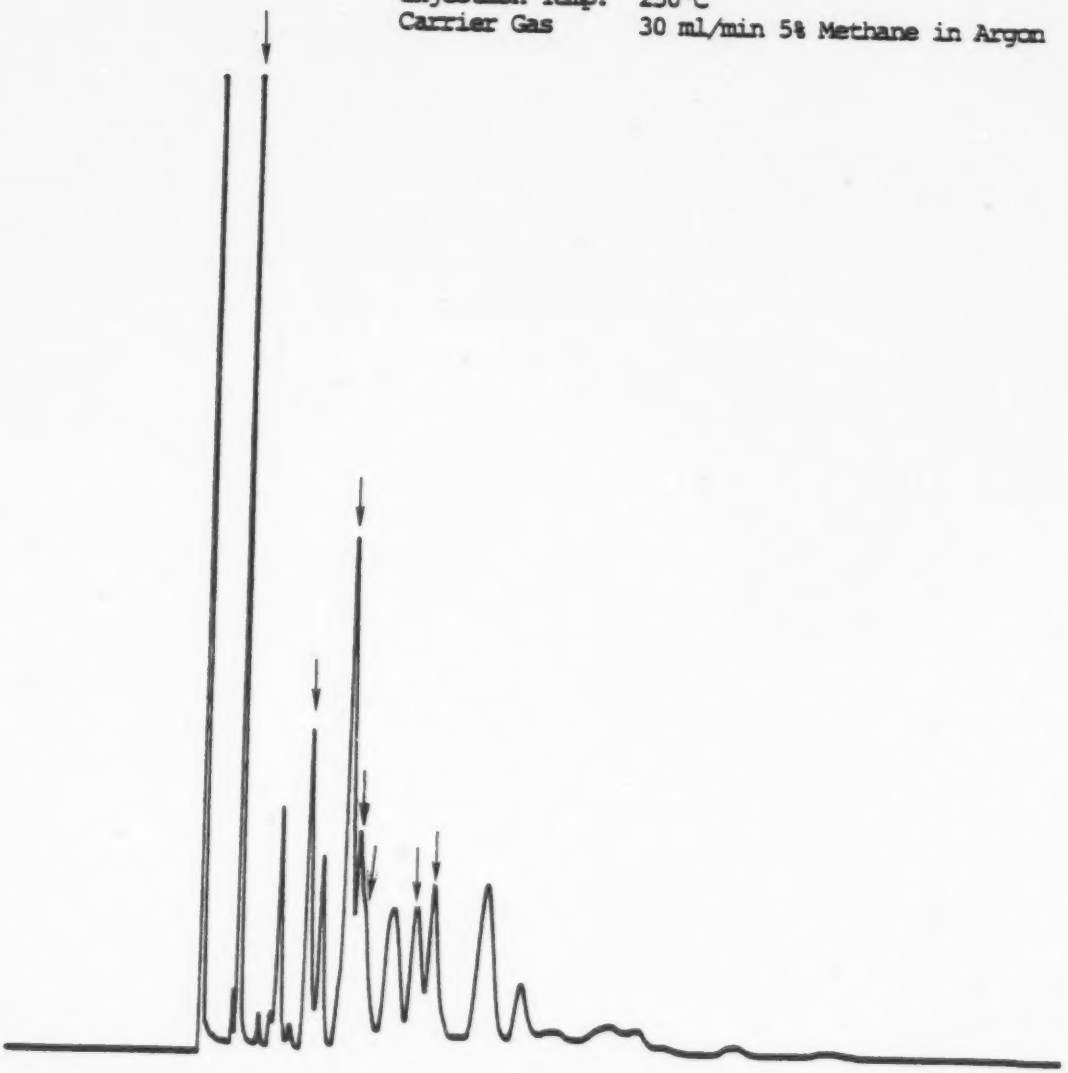


FIGURE B8. HYDRAULIC FLUID (Peaks Used For Quantitation)

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	220°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

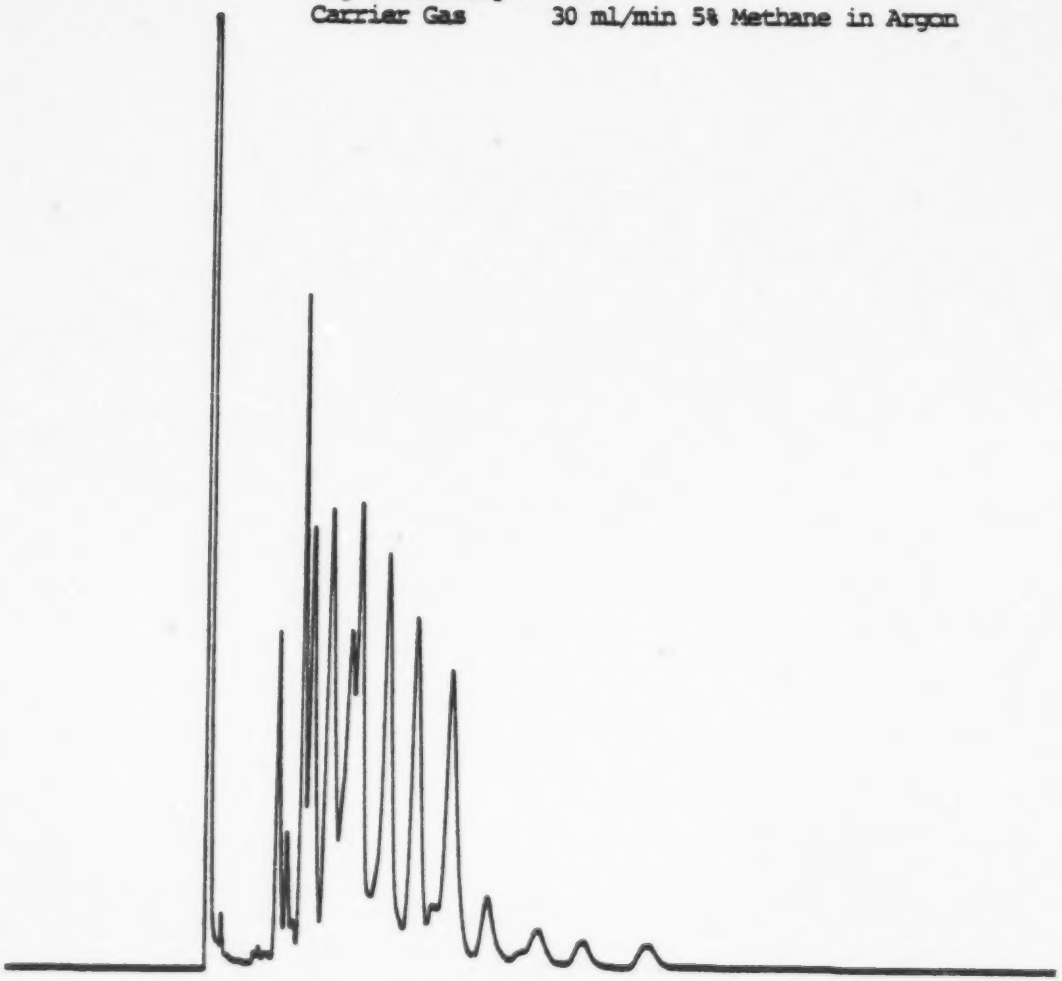


FIGURE B9. AROCLOR 1254 STANDARD CHROMATOGRAM

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	220°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

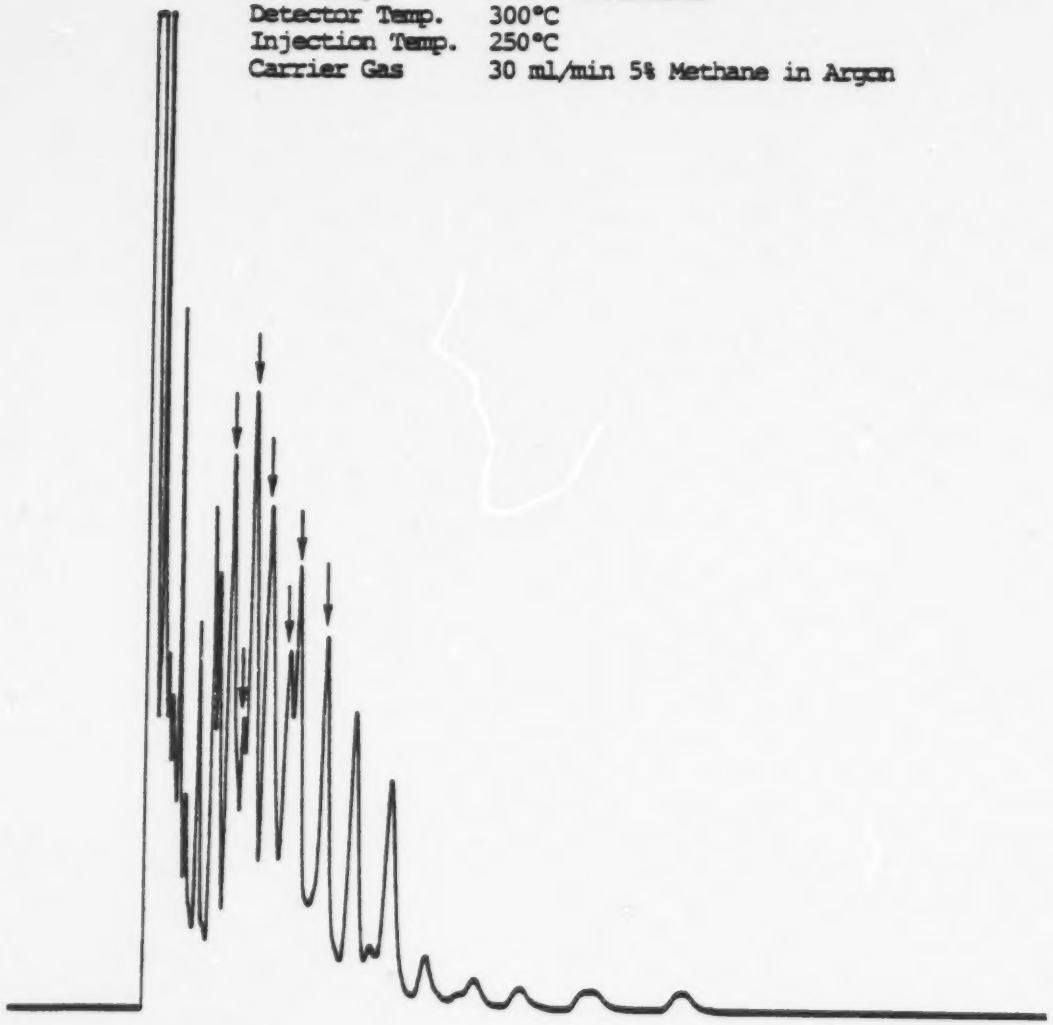
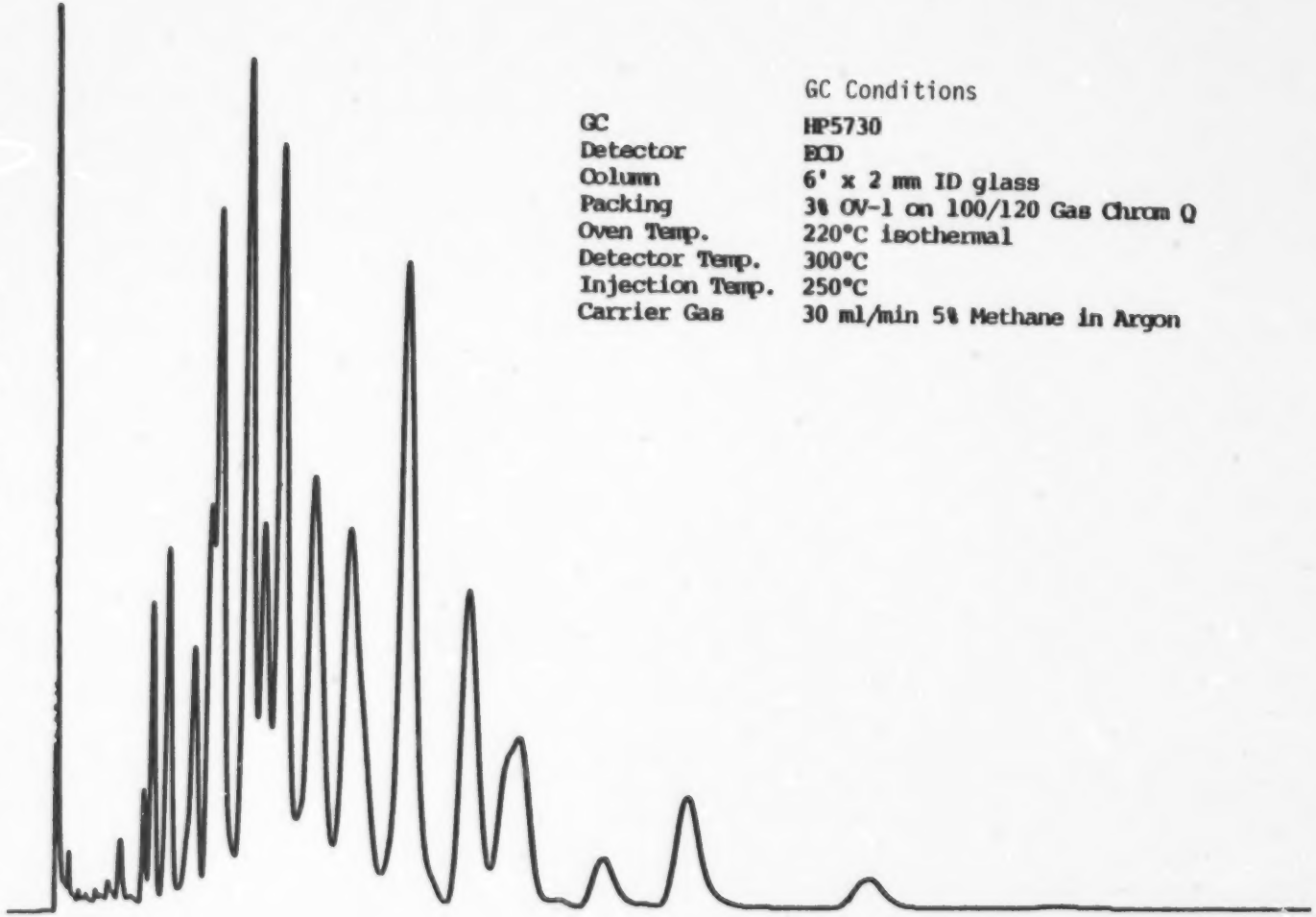


FIGURE B10. WASTE OIL (Peaks Used For Quantitation)



GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	220°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

FIGURE B11. AROCLOR 1260 STANDARD

GC Conditions

GC	HP5730
Detector	ECD
Column	6' x 2 mm ID glass
Packing	3% OV-1 on 100/120 Gas Chrom Q
Oven Temp.	220°C isothermal
Detector Temp.	300°C
Injection Temp.	250°C
Carrier Gas	30 ml/min 5% Methane in Argon

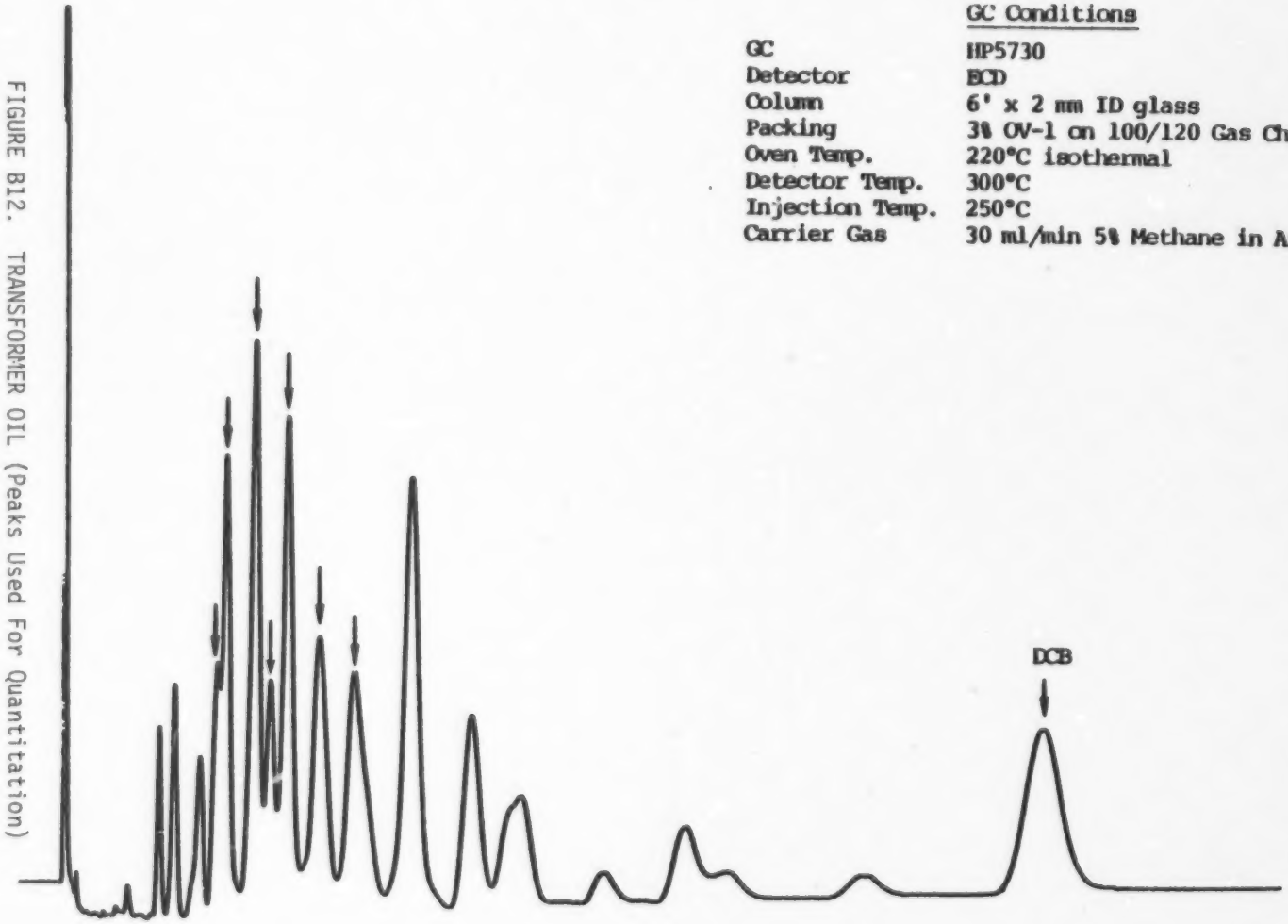


FIGURE B12. TRANSFORMER OIL (Peaks Used For Quantitation)

APPENDIX C

INSTRUMENTS USED BY PARTICIPATING LABORATORIES

Lab No.	ECD	HECD		
	GC Model With ECD	GC Model	Detector Model	Reactor Temp
1	No Lab			
2	NP	No HECD		
3	Tracor 560	Tracor 560	700A	---- NP
4	Tracor 560	Tracor 570	700A	---- NP
5	P-E Sigma 1	Varian 3700	700A	---- NP
6	No Lab			
7	P-E Sigma 1	Tracor 560	700A	---- NP
8	No Lab			
9	Tracor 560	Tracor 560	700A	---- NP
10	Tracor 560	Tracor 560	700A	---- NP
11	Tracor 560	Tracor 560	?	900°C
12	Tracor MT220	Tracor 570	700	950°C
13	Tracor 560	Tracor 560	700A	---- NP
14	HP 5880A	HP 5750	700	---- NP
15	Tracor 560	Tracor 560	700A	---- NP
16	Varian 3700	HP 5713A	310	---- NP
17	NP	No HECD		
18	Tracor 560	Tracor 560	?	920°C
19	HP 5840A	Varian 3700	700A	---- NP
20	Varian 1400	Tracor 560	700A	---- NP
21	No Lab			
22	NP	P-E 881	?	950°C
23	Varian 3700	Varian 3700	?	---- NP
24	Varian 3700	Tracor 560	700A	950°C

NP = Not Provided.

APPENDIX D

RAW DATA

This appendix contains the raw data obtained from the participating laboratories. The data are arranged by laboratory to facilitate evaluation of intralaboratory data. Interlaboratory data are compared in the statistics generated for methods evaluation and comparison.

All non-definitive data ("less than" and "none detected") are converted to zeroes for statistical evaluation and computations. All outlier data (laboratory outlier or individual outlier) are designated by an asterisk after the data entry in the tables.

It is also noted that laboratory numbers 1, 6, 8, and 21 were not assigned, laboratory #17 analyzed all samples by ECD only, and laboratory #2 analyzed only waste oil by ECD.

TABLE D-1.

RAW DATA FOR AROCLOR 1016 IN CAPACITOR FLUID BY HECD

RAW DATA FOR CAPACITOR 1016 IN HECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		33.70	492.00	114.00	81.60	441.00	41.80
1		27.00	110.00*	65.00	72.00	450.00	40.00
4		25.80	438.00	97.50	71.30	360.00	35.70
5		40.00	474.00	127.00	98.00	402.00	47.00
8		36.00	360.00	10.00	250.00*	420.00	21.00
9		35.00	227.00	135.00	93.00	183.00	47.00
10		26.00	340.00	99.00	61.00	360.00	34.00
11		23.00	320.00	820.00*	55.00	270.00	29.00
12		40.00	516.00	75.00	75.00	405.00	39.00
13		28.00	460.00	130.00	65.00	450.00	31.00
14		18.00	458.00	48.00	48.00	377.00	23.00
15		40.00	310.00	75.00	53.00	270.00	20.00
16		28.00	490.00	95.00	81.00	440.00	43.00
17							
18		39.00	450.00	140.00	68.00	430.00	58.00
19	*	14.20*	110.00*	39.80*	28.60*	182.00*	19.30*
20		30.00	480.00	100.00	71.00	420.00	37.00
22		22.00	440.00	120.00	79.00	320.00	42.00
23		38.00	500.00	110.00	80.00	450.00	42.00
24		23.00	560.00	110.00	79.00	490.00	35.00

* = REJECTED

LT = CONCENTRATION, DT = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-2.

RAW DATA FOR AROCLOR 1016 IN CAPACITOR FLUID BY ECD

RAW DATA FOR CAPACITOR 1016 IN ECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		33.70	492.00	114.00	81.60	441.00	41.80
3	*	11.80*	220.00*	60.00*	30.60*	317.00*	18.40*
4		37.30	513.00	135.00	97.00	451.00	48.40
5		40.00	492.00	117.00	86.00	435.00	45.00
7	*	120.00*	480.00*	200.00*	320.00*	530.00*	120.00*
9		35.00	263.00	114.00	79.00	640.00	45.00
10		34.00	460.00	103.00	74.00	370.00	31.00
11		22.00	320.00	75.00	54.00	310.00	26.00
12		42.00	311.00	92.00	77.00	303.00	48.00
13		35.00	460.00	110.00	81.00	430.00	40.00
14	*	74.00*	752.00*	199.00*	130.00*	641.00*	83.00*
15		30.00	320.00	20.00	40.00	290.00	20.00
16		38.00	390.00	88.00	81.00	25.00	25.00
17		32.00	410.00	110.00	72.00	370.00	37.00
18		14.00	630.00	84.00	34.00	660.00	19.00
19	*	10.20*	175.00*	34.80*	31.50*	163.00*	16.20*
20		40.00	460.00	110.00	77.00	400.00	29.00
22		26.00	440.00	92.00	66.00	390.00	48.00
23	*	41.00*	780.00*	166.00*	130.00*	770.00*	65.00*
24		27.00	190.00	46.00	40.00	190.00	23.00

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-3.

RAW DATA FOR AROCLOR 1242 IN HYDRAULIC FLUID BY HECD

RAW DATA FOR HYDRAULIC 1242 IN HECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		492.00	95.70	47.10	39.80	64.30	402.00
3		350.00	64.00	26.00	50.00	60.00	350.00
4		560.00	91.00	31.60	27.50	45.60	378.00
5		494.00	86.00	36.00	36.00	57.00	371.00
7	*	110.00*	24.00*	16.00*	16.00*	27.00*	92.00*
9		340.00	77.00	32.00	27.00	56.00	270.00
10		460.00	94.00	40.00	34.00	61.00	400.00
11		380.00	65.00	28.00	24.00	43.00	300.00
12		430.00	76.00	38.00	37.00	59.00	361.00
13		470.00	88.00	36.00	36.00	67.00	410.00
14	*	386.00*	45.00*	20.00*	19.00*	36.00*	337.00*
15		480.00	40.00	42.00	41.00	58.00	390.00
16		410.00	80.00	20.00	33.00	55.00	360.00
17							
18		460.00	64.00	25.00	27.00	43.00	370.00
19	*	776.00*	82.30*	66.50*	83.50*	75.60*	607.00*
20		460.00	85.00	37.00	33.00	55.00	370.00
22		450.00	58.00	32.00	39.00	43.00	350.00
23		440.00	100.00	40.00	41.00	60.00	410.00
24		440.00	74.00	30.00	31.00	56.00	320.00

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-4.

RAW DATA FOR AROCLOR 1242 IN HYDRAULIC FLUID BY ECD

RAW DATA FOR HYDRAULIC 1242 IN ECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		492.00	95.70	47.10	39.80	64.30	402.00
3		487.00	80.60	40.30	37.80	62.10	397.00
4		555.00	80.00	36.20	39.20	60.00	425.00
5		475.00	84.00	30.00	30.00	54.00	300.00
7		190.00*	190.00*	20.00	18.00	38.00	180.00*
9	*	325.00*	60.00*	27.00*	25.00*	43.00*	175.00*
10		400.00	87.00	21.00	18.00	50.00	330.00
11		390.00	78.00	34.00	33.00	56.00	340.00
12		403.00	89.00	32.00	32.00	68.00	350.00
13		450.00	82.00	36.00	37.00	100.00	350.00
14	*	735.00*	149.00*	66.00*	64.00*	102.00*	580.00*
15		380.00	90.00	50.00	40.00	90.00	370.00
16		430.00	60.00	28.00	27.00	43.00	240.00
17		410.00	100.00	40.00	39.00	67.00	370.00
18		500.00	45.00	14.00	13.00	36.00	390.00
19	*	697.00*	103.00*	56.10*	74.60*	69.20*	627.00*
20		510.00	89.00	39.00	44.00	59.00	380.00
22		400.00	59.00	29.00	32.00	49.00	320.00
23		530.00	97.00	41.00	38.00	69.00	390.00
24		480.00	79.00	38.00	33.00	49.00	360.00

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-5.

RAW DATA FOR 2-MCB IN HYDRAULIC FLUID BY HECD

RAW DATA FOR HYDRAULIC 2-MCB IN HECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		1018.00	438.00	55.60	41.30	350.00	847.00
3		980.00	380.00	10.00	25.00	330.00	930.00
4		1114.00	375.00	31.30	30.50	259.00	980.00
5		1247.00	272.00	44.00	38.00	147.00*	1055.00
7	*	1600.00*	610.00*	91.00*	56.00*	340.00*	1200.00*
9		856.00	545.00	47.00	5.60*	358.00	800.00
10		820.00	480.00	33.00	32.00	380.00	710.00
11	*	740.00*	320.00*	26.00*	22.00*	230.00*	670.00*
12		1089.00	482.00	34.00	34.00	330.00	902.00
13	*	1900.00*	960.00*	69.00*	65.00*	670.00*	1800.00*
14	*	751.00*	302.00*	16.00*	16.00*	116.00*	691.00*
15		870.00	130.00	30.00	30.00	260.00	780.00
16		1100.00	440.00	30.00	30.00	310.00	870.00
17							
18		1000.00	380.00	33.00	28.00	280.00	860.00
19		1590.00*	510.00	62.00	65.30*	269.00	885.00
20		960.00	430.00	32.00	29.00	280.00	790.00
22		1000.00	470.00	36.00	34.00	300.00	790.00
23		1100.00	260.00	31.00	28.00	390.00	890.00
24		920.00	440.00	32.00	30.00	330.00	860.00

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-6

RAW DATA FOR 2-MCB IN HYDRAULIC FLUID BY ECD

RAW DATA FOR HYDRAULIC 2-MCB IN ECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		1018.00	438.00	55.60	41.30	350.00	847.00
3		821.00	388.00	38.70	40.00	309.00	706.00
4		886.00	368.00	33.20	39.20	280.00	837.00
5		1286.00	236.00	44.00	40.00	152.00	984.00
7		1800.00	620.00	50.00	5.00	56.00	1800.00♦
9		750.00	372.00	39.00	35.00	330.00	765.00
10		830.00	380.00	22.00	16.00	300.00	740.00
11		650.00	300.00	25.00	22.00	220.00	520.00
12		890.00	550.00	44.00	54.00	307.00	1038.00
13	♦	1900.00♦	840.00♦	75.00♦	70.00♦	590.00♦	1600.00♦
14	♦	1759.00♦	852.00♦	101.00♦	87.00♦	598.00♦	1467.00♦
15		380.00	90.00	50.00	40.00	92.00	370.00
16		710.00	300.00	28.00	27.00	200.00	760.00
17		900.00	460.00	38.00	34.00	330.00	813.00
18		1300.00	450.00	21.00	19.00	380.00	1100.00
19		1720.00	480.00	54.50	69.50	248.00	830.00
20		960.00	450.00	26.00	26.00	330.00	870.00
22		670.00	330.00	54.00	56.00	260.00	540.00
23	♦	470.00♦	180.00♦	2.70♦	6.00♦	118.00♦	360.00♦
24		980.00	430.00	34.00	28.00	300.00	800.00

♦ = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-7.

RAW DATA FOR AROCLOR 1260 IN TRANSFORMER OIL BY HECD

RAW DATA FOR TRANSFORMER 1260 IN HECD

		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		332.00	68.50	38.70	392.00	80.70	32.50
LAB/AN	LAB REJECTED						
3		220.00	33.00	35.00	365.00	54.00	6.00
4		348.00	60.60	63.00	816.00*	121.00	52.00
5		325.00	69.00	34.00	380.00	79.00	30.00
7	*	170.00*	30.00*	33.00*	210.00*	71.00*	21.00*
9		400.00	83.00	48.00	430.00	100.00	36.00
10		320.00	93.00	36.00	400.00	94.00	35.00
11		290.00	57.00	34.00	320.00	75.00	29.00
12		293.00	51.00	29.00	360.00	60.00	27.00
13		220.00	72.00	36.00	380.00	79.00	32.00
14		332.00	54.00	29.00	306.00	45.00	18.00
15		360.00	87.00	46.00	530.00	97.00	36.00
16		350.00	51.00	33.00	380.00	73.00	29.00
17							
18	*	580.00*	94.00*	52.00*	620.00*	100.00*	39.00*
19		510.00	62.30	38.60	599.00*	99.30	12.80
20		310.00	65.00	36.00	390.00	76.00	30.00
22		360.00	69.00	35.00	430.00	72.00	29.00
23		320.00	69.00	70.00	440.00	84.00	36.00
24		390.00	66.00	30.00	400.00	101.00	22.00

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-8.

RAW DATA FOR AROCLOR 1260 IN TRANSFORMER OIL BY ECD

RAW DATA FOR TRANSFORMER 1260 IN ECD

		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		332.00	68.50	38.70	392.00	80.70	32.50
LAB/AN	LAB REJECTED						
3		301.00	72.60	58.70♦	363.00	81.30	32.20
4		475.00	58.20	34.40	758.00♦	90.00	32.30
5		324.00	69.00	38.00	381.00	79.00	31.00
7	♦	180.00♦	60.00♦	30.00♦	280.00♦	56.00♦	17.00♦
9		400.00	32.00♦	0.00♦	125.00♦	34.00♦	15.00
10		350.00	84.00	41.00	380.00	100.00	35.00
11		340.00	73.00	40.00	400.00	81.00	33.00
12		286.00	70.00	33.00	316.00	78.00	21.00
13		330.00	55.00	32.00	380.00	64.00	22.00
14	♦	430.00♦	97.00♦	53.00♦	506.00♦	109.00♦	43.00♦
15		360.00	80.00	40.00	420.00	76.00	40.00
16		290.00	60.00	32.00	350.00	69.00	25.00
17		300.00	65.00	34.00	360.00	72.00	27.00
18		330.00	64.00	32.00	400.00	74.00	24.00
19		443.00	70.40	30.80	468.00	88.00	23.80
20		310.00	73.00	43.00	420.00	100.00	24.00
22		330.00	64.00	38.00	380.00	77.00	31.00
23	♦	280.00♦	18.00♦	24.00♦	320.00♦	58.00♦	15.00♦
24		310.00	75.00	42.00	370.00	87.00	32.00

♦ = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-9.

RAW DATA FOR DCB IN TRANSFORMER OIL BY HECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		11.20	3.86	0.55	16.60	5.71	0.37
3		10.00	3.60	0.84	24.00	7.00	0.60
4		21.00	3.00	0.55	24.00	7.43	0.31
5		11.00	4.00	0.60	15.00	5.00	0.50
7		480.00*	1.40	0.77	6.80	1.60	0.63
9		94.00	31.00	0.50	165.00*	54.00*	0.30
10		22.00	5.20	0.54	27.00	7.30	0.29
11		8.10	2.70	0.44	12.00	4.30	0.34
12		11.00	3.40	0.38	13.00	5.30	0.84
13		8.80	3.60	0.49	14.00	5.00	0.31
14		72.00	24.00	0.17	56.00*	42.00*	0.22
15		18.00	7.00	0.58	29.00	9.00	0.43
16		10.00	3.40	< 1.00*	13.00	4.60	< 1.00*
17							
18		< 25.00*	< 25.00*	0.55	< 25.00*	< 25.00*	0.45
19		5.60	25.20	1.00	19.60	0.00*	0.70
20		10.00	3.20	0.55	14.00	4.80	0.29
22		11.00	4.00	0.77	16.00	5.30	0.99
23		66.00	16.00	0.11	76.00*	29.00*	0.10
24		13.00	< 5.00*	0.50	19.00	9.00	0.40

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-10.

RAW DATA FOR DCB IN TRANSFORMER OIL BY ECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		11.20	3.86	0.55	16.60	5.71	0.37
3		13.00	4.83	0.97	19.40	6.87	0.45
4		13.10	3.93	0.00♦	23.60	5.25	0.00♦
5		12.00	4.00	0.50	17.00	6.00	0.40
7		1.70	5.00	0.05	3.00	1.20	0.12
9		97.00♦	30.00	0.00♦	99.00♦	46.00♦	10.00♦
10		12.00	4.90	0.60	17.00	6.50	0.45
11		9.10	3.30	0.50	14.00	4.70	0.36
12		11.00	4.50	0.75	17.00	5.00	0.36
13		8.60	3.10	0.32	13.00	4.50	< 1.00♦
14		18.00	5.20	0.80	22.00	7.40	0.50
15		20.00	10.00	0.00♦	30.00	10.00	0.00♦
16		8.80	3.40	0.75	15.00	5.70	0.54
17		12.00	4.10	0.60	17.00	5.70	0.40
18		11.00	3.70	0.58	17.00	5.20	0.26
19		9.40	28.20	4.00♦	11.30	4.30	0.30
20		10.00	3.80	< 1.00♦	16.00	5.20	< 1.00♦
22		7.70	1.10	0.20	75.00♦	1.80	0.10
23		58.00♦	23.00	4.60♦	79.00♦	16.00♦	0.00♦
24		14.00	5.00	0.80	19.00	6.60	0.50

♦ = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-11.

RAW DATA FOR AROCLOR 1254 IN WASTE OIL BY HECD

LAB/AN	LAB REJECTED	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		350.00	56.10	38.60	71.70	461.00	46.90
2	*	*	*	*	*	*	*
3		150.00	20.00	40.00	25.00	150.00*	15.00
4		375.00	45.00	24.40	40.00	470.00	30.00
5		348.00	40.00	29.00	54.00	391.00	27.00
7		170.00	46.00	48.00	66.00	17.00*	55.00
9		320.00	52.00	34.00	70.00	450.00	39.00
10		270.00	43.00	39.00	67.00	370.00	43.00
11		300.00	68.00	24.00	48.00	400.00	28.00
12		210.00	34.00	26.00	43.00	357.00	34.00
13		310.00	50.00	39.00	87.00	400.00	36.00
14	*	230.00*	18.00*	13.00*	29.00*	275.00*	16.00*
15		340.00	30.00	20.00	8.00	420.00	20.00
16		310.00	61.00	45.00	67.00	420.00	52.00
17							
18		360.00	42.00	43.00	68.00	410.00	48.00
19		542.00*	30.50	18.20	68.30	465.00	40.30
20		310.00	31.00	21.00	38.00	420.00	24.00
22		290.00	55.00	34.00	25.00	440.00	30.00
23		270.00	62.00	45.00	71.00	460.00	58.00
24		250.00	37.00	< 25.00*	51.00	310.00	31.00

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01

TABLE D-12.

RAW DATA FOR AROCLOR 1254 IN WASTE OIL BY ECD

		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6
INCREMENT IN UG/G		350.00	56.10	38.60	71.70	461.00	46.90
LAB/AN	LAB REJECTED						
2		350.00	47.00	29.00	64.00	430.00	38.00
3		328.00	50.00	36.00	68.00	457.00	46.00
4		396.00	47.60	39.00	33.60	501.00	42.70
5		359.00	44.00	34.00	62.00	409.00	33.00
7		300.00	24.00	20.00	39.00	380.00	41.00
9		305.00	50.00	33.00	61.00	395.00	45.00
10		270.00	54.00	35.00	63.00	420.00	37.00
11		370.00	54.00	36.00	63.00	460.00	47.00
12	*	184.00*	24.00*	30.00*	55.00*	330.00*	25.00*
13		310.00	46.00	30.00	62.00	420.00	39.00
14	*	890.00*	89.00*	51.00*	102.00*	461.00*	67.00*
15		390.00	60.00	40.00	70.00	450.00	40.00
16		38.00*	300.00*	17.00	57.00	410.00	22.00
17		350.00	54.00	33.00	71.00	480.00	40.00
18		360.00	46.00	32.00	88.00	360.00	27.00
19		558.00*	35.40	26.20	56.10	466.00	28.10
20		360.00	44.00	31.00	62.00	470.00	37.00
22	*	160.00*	32.00*	26.00*	26.00*	380.00*	32.00*
23		250.00	28.00	20.00	38.00	440.00	35.00
24		260.00	39.00	28.00	53.00	350.00	31.00

* = REJECTED

CT = CONCENTRATION, DM = DIFFERENT METHOD, IM = IMPROPER METHOD, UD = UNACCEPTABLE DATA, < = LESS THAN

CURRENT SIGNIFICANCE LEVELS
1. LAB RANKING DATA REJECTION TESTS, ALPHA =0.05
2. INDIVIDUAL OUTLIER TESTS USING THOMPSON(S) RULE, ALPHA = .05
3. INDIVIDUAL OUTLIER USING 4 X STD DEV LIMITS, ALPHA LESS THAN .01
4. INDIVIDUAL OUTLIER USING STUDENTS T X STD DEV LIMITS, ALPHA =0.01